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A Study of the Initial Phase of the Aqueous Chlorination of Kraft Pulp Meals

Norman A. Russell

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A STUDY OF THE INITIAL PHASE OF THE AQUEOUS CHLORINATION OF KRAFT PULP MEALS

A thesis submitted by

Norman A. Russell

B.S. 1960, North Carolina State University
M.S. 1962, Lawrence College

in partial fulfillment of the requirements
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Appleton, Wisconsin

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SUMMARY

The initial phase of the aqueous chlorination of two kraft pulp meals was investigated. A tubular flow reactor was constructed to attain reaction times of less than one minute. This technique was required since the time involved in sampling batch systems can be large in comparison to the desired reaction time. Pulp meals were used to minimize the formation of a fiber plug in the reaction stream. Duplicate chlorination runs showed the reproducibility of the reactor system to be quite good. The agreement between duplicate experiments was not affected by drastic changes in the reaction conditions, in the reaction duration, or in the flow rate at constant reaction time.

The most influential process variable was pH. Its importance was derived from its effect on the extent of bound chlorine in the pulp. The level of bound chlorine was related to the extent of lignin removal. Increased applications of chlorine promoted delignification when molecular chlorine was present. Hypochlorous acid alone did not yield significant delignification beyond an initial loss of lignin. The dependence of lignin removal on chlorine concentration changed rapidly in the early phase of reaction.

Approximately 50% of the total chlorine consumption was attributed to oxidation reactions and about one gram of chlorine was consumed per gram of lignin removed from the pulp.

The lowering of the reaction temperature decreased lignin removal apparently through a reduction of the extent of oxidation. The levels of chlorine bound by the pulp were not substantially altered by temperature variations.

Chlorination of a second kraft pulp meal having a higher initial lignin content indicated that the course of delignification for both pulps was similar. However, the relationships between bound chlorine and lignin removal for the two

pulps were somewhat different. The accessibility of lignin in the two pulps was believed to be the cause of the observed differences.

Cellulose degradation, as indicated by pulp viscosity, was relatively low except at a reaction pH of 1.3. The drastic viscosity loss observed in this case resulted from chlorine attack and acid hydrolysis. Lower chlorine concentrations and reaction temperatures reduced the extent of viscosity loss. Little or no change of viscosity with increasing reaction time was measured.

An empirical rate expression was evaluated. A reaction order with respect to lignin was determined by graphical integration of selected delignification curves. It was found that the order ranged from 1.6 to 2.0 depending upon the pulp and the reaction conditions employed. The experimental results indicated a complex concentration term involving both molecular chlorine and hypochlorous acid would be required to describe chlorination in its initial phase.

INTRODUCTION

Bleaching is an important phase in the production of kraft pulps for a great variety of uses. The treatment of a pulp with acidic, aqueous solutions of chlorine is a basic step in this operation. In a sense, aqueous chlorination is not a true bleaching process as it yields no color improvement. However, this treatment does result in the solubilization of lignin in water and alkali. This additional delignification after the digestion of a pulp is desirable in that lignin and its derivatives are believed to be the principal sources of color in kraft pulps (1-5). These last traces of lignin cannot be removed easily in the digestion process without serious losses of carbohydrates as well (6,7). On the other hand, proper application of aqueous chlorine can solubilize lignin with little concurrent carbohydrate degradation. As a result, this treatment is of considerable interest and importance in the bleaching of kraft pulps.

PRESENTATION OF THE PROBLEM

Due to the complexity of the reaction system, elucidation of interactions between aqueous chlorine and pulp is incomplete. However, many studies have been directed toward this goal. The trends in chemical consumption and delignification observed in these investigations are illustrated in Fig. 1. It is seen that both chlorine consumption and lignin removal exhibit an initial, rapid phase followed by a slower reaction phase.

Consumptions ranging from 50 to 90% of the applied chlorine have been observed in the first 3 to 5 minutes of reaction (8-11). Concurrent rapid delignification has been reported also (10-13). It would appear then that the early phase of pulp chlorination is of major importance; however, the initial stage of this treatment has yet to be examined directly. As a result, the present study was initiated to investigate the first minute of chlorination. Emphasis was placed on the influence of selected process variables in regard to the rate, extent, and nature of kraft pulp delignification by aqueous chlorination.

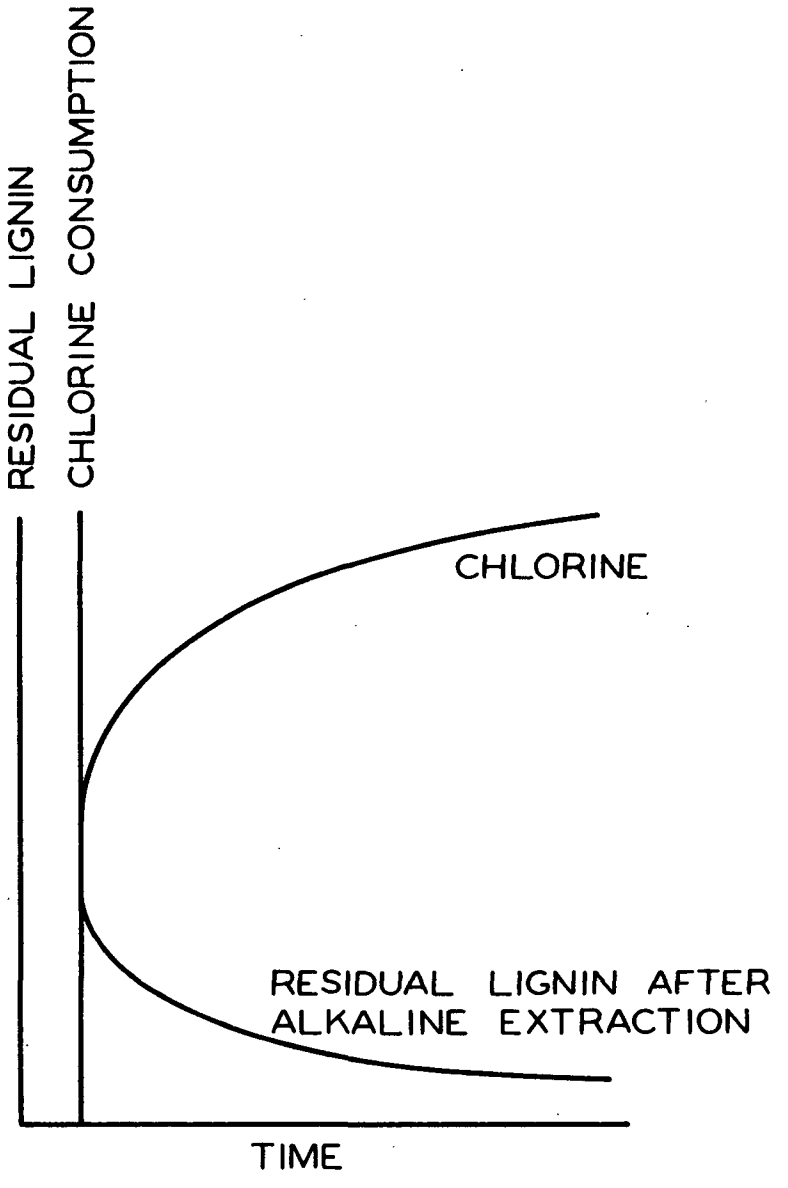


Figure 1. Trends in Pulp Chlorination (8)

LITERATURE SURVEY

In the following paragraphs, three important facets of aqueous chlorination are discussed in terms of pertinent literature.

AQUEOUS CHLORINE SOLUTIONS

The hydrolysis of chlorine is a key consideration in pulp chlorination.

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$$

This reaction is known to be extremely rapid (14-16). In acidic solutions, hydrochloric acid is dissociated while hypochlorous acid is not.

The hydrolysis equilibrium is expressed as follows:

$$K_H = [HOCl]\,[H^+]\,[Cl^-] \,/\, [Cl_2]\,[H_2O]$$

It is seen in this equation that the relative proportions of molecular chlorine (Cl_2) and hypochlorous acid (HOCl) in a solution can be altered by pH variations and dilution. Furthermore, K_H is temperature dependent as shown in Table I.

TABLE I

TEMPERATURE DEPENDENCE OF HYDROLYSIS EQUILIBRIUM CONSTANT (17)

$K_H \times 10^{-4}$	Temperature, °C.
1.46	0
2.81	15
3.94	25
5.10	35
6.05	45

AQUEOUS CHLORINATION OF PULP

It is well known that aqueous chlorine can substitute and oxidize organic compounds. The relative rates of these two reactions have led investigators to believe that the initial, rapid phase of chlorination is dominated by lignin substitution, and the slower phase primarily involves oxidative degradation reactions (18-20). For each mole of chlorine consumed, substitution reactions yield one mole of hydrochloric acid and oxidation reactions produce two moles of hydrochloric acid. These relationships have been utilized to estimate the relative consumptions of chlorine by the two reactions (11, 12, 21). An example of such an estimation is presented in Fig. 2.

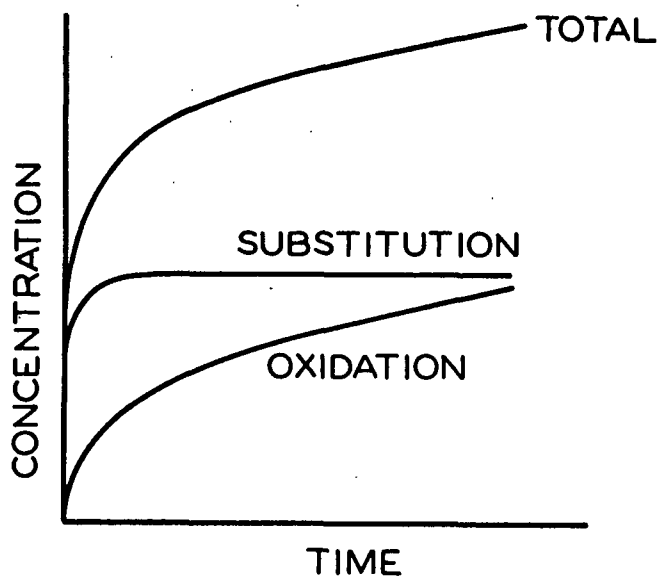


Figure 2. Chlorine Consumption in Pulp Chlorination (11)

It is seen that both consumptions are rapid initially with substitution occurring more extensively. Substitution ceases after a relatively short time; while oxidation proceeds over a much longer period. Giertz (18) has stated that both substitution and oxidation are required to reach optimum delignification of a kraft pulp.

As noted previously, aqueous chlorine treatments serve to make lignin potentially soluble in water and alkali. Therefore, chlorination must be accompanied by an extraction of the lignin degraded by chlorine attack. It has been found that of the lignin degraded by chlorination, about 50% can be removed by hot water and the remainder must be extracted with alkali (12,18). Both Giertz (11) and Grangaard (21) have stated that diffusion is the most important aspect of lignin removal in the extraction of a chlorinated pulp. Apparently, some chemical reaction is occurring in this step since consumption of alkali in the extraction step has been reported as well as removal of chlorine from isolated "chlorolignins" (12,22,23). It is interesting to note that Arnold, Simmons, and Curran (24) found no apparent relationship between the ease of alkali solubilization of wood and kraft pulp lignin and the chlorine content of the lignin.

Delignification by aqueous chlorine is not accomplished without some concurrent degradation of the cellulose fraction of a pulp. Pulp viscosity has been employed as a measure of such degradation. It has been found that viscosity losses were greatest in the early stages of pulp chlorination (13,19). Also, the magnitude of this initial loss is dependent on the viscosity of the original pulp; it was found that increased original viscosities yielded greater initial viscosity losses (11). Along the same line, kraft pulps have been

found to exhibit greater viscosity losses than sulfite pulps in mill chlorinations (25).

The hot alkali solubility of a pulp has also been used as a measure of the carbohydrate degradation. Hisey and Koon (26) showed this solubility to be low with pulps chlorinated below pH 4.9. Sharp drops in viscosity and increases in hot alkali solubility are observed when the reaction pH approaches neutrality (25,26).

This phase of the literature review indicated the most important operating variables are temperature, time, pH, lignin content, and chlorine concentration. Sulfite pulps have received considerably more attention. As a result, specific data describing the response of kraft pulp to chlorination at reaction times above several minutes is limited and absent altogether for shorter reaction times. When available, pertinent literature concerning the effects of these variables is presented in the discussion of the results of the present system.

CHLORINATION OF MODEL SYSTEMS

The basic reaction mechanisms by which lignin is removed and cellulose is degraded are difficult to examine in studies of pulp chlorination. For this reason, "isolated" lignins and model compounds of cellulose and lignin have been investigated to gain some insight into the pulp – chlorine reaction system.

LIGNIN MODEL SYSTEMS

In this discussion, it is assumed that the basic lignin unit is an aromatic nucleus with a propyl side chain as shown in Fig. 3.

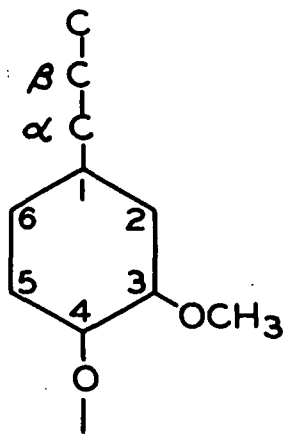


Figure 3. Lignin Representation

The results of numerous studies indicate substitution of chlorine may occur at many sites within the lignin complex. Substitution at Position 6 (see Fig. 3) appears to be a general reaction in the chlorination of lignin-like compounds (27,28). It was noted that the substituents on the aromatic nuclei of such compounds as veratryl and vanillyl alcohols enhance chlorine substitution at this point (28). This type of substitution should not increase the solubility of lignin (28).

A second substitution involving "chain displacement" has been observed for both chlorine and bromine (28-30). This reaction is designated as a displacement reaction to distinguish it from the substitution of chlorine for hydrogen on the aromatic nucleus. The general occurrence of this reaction is illustrated in Fig. 4.

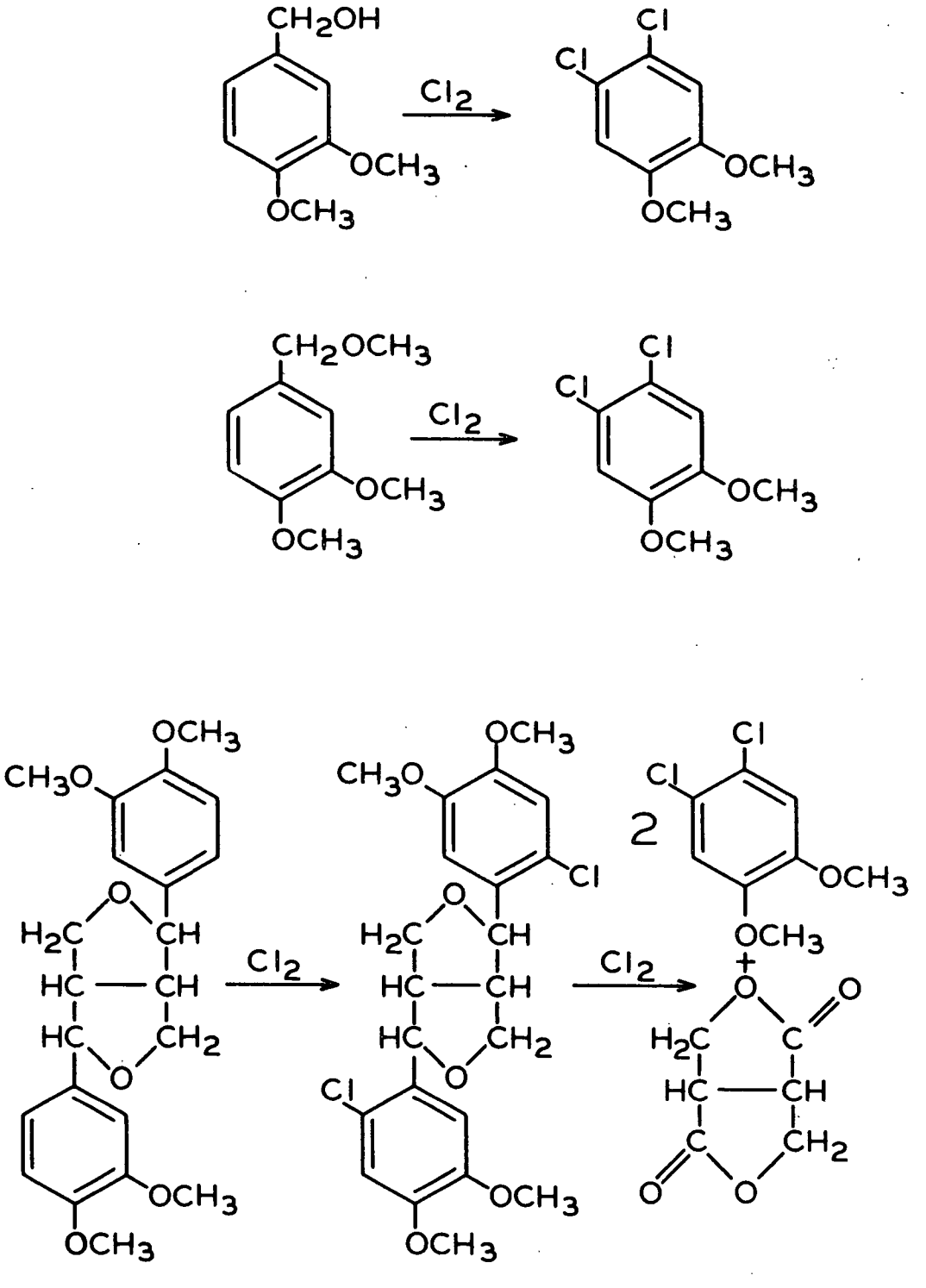
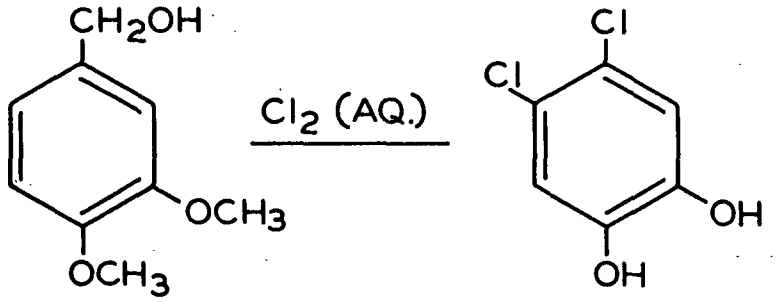


Figure 4. Displacement Reactions

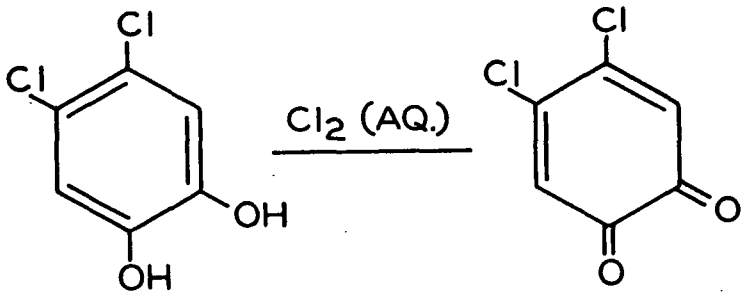
A similar displacement of the propyl side chain at the one-position in Fig. 3 would result in lignin degradation. The displacement reaction competes with substitution of the nucleus (28,30). It has been reported that the former reaction is about one-tenth as rapid as the latter in the chlorination of veratryl alcohol (28). Alcoholic and ether groups on the α-carbon of the propyl side chain enhance displacement (see Fig. 3). In addition, carbonyl and carboxyl groups in the α-position can be displaced when a hydroxyl group is located para to the side chain (31). It is apparent from these studies that the displacement reaction may be of importance in lignin degradation and its extent is influenced by the nature of both the aromatic ring and the side chain attached to it.

Free phenolic hydroxyls may enhance ortho substitution as well. In terms of the lignin representation, a hydroxyl in the four-position would favor substitution at the five-position. Studies performed by Shorygina (32), Migita (33), and their co-workers indicate substitution of the side chain may occur also. Shorygina found evidence that ring substitution is more rapid.

Rapid demethylation has been observed in studies of lignin model compounds, isolated lignin, and lignin in wood or pulp when aqueous chlorine is applied (22,27,28,34,35). This reaction results in the replacement of a methoxyl group by a hydroxyl group as shown in Fig. 5. The available evidence indicates dealkylation is a chlorine-catalyzed hydrolysis of the alkylaryl ether bonds (28,34). This reaction is hindered by chlorine substitution ortho to the alkoxyl group (28,34,35). It has been suggested that a similar hydrolysis of ether linkages in the lignin structure (see Position four in Fig. 3) could contribute to lignin solubilization. In this respect, it is interesting to note that extensive cleavage of phenolic ether bonds is thought to occur in kraft pulping (36); therefore, the importance of chlorine-hydrolyzed cleavage of such bonds may be minor.



DEMETHYLATION



OXIDATION

Figure 5. Demethylation and Oxidation

Oxidative attack of phenolic compounds, such as demethylated lignin, results in quinone formation and in destruction of the ring structure (27,28). The color developed in a pulp during chlorination has been attributed to the production of quinoid structures in the oxidation of lignin (37).

CELLULOSE MODEL SYSTEMS

Dyfverman and co-workers (38) treated methyl β-D-glucopyranoside with aqueous chlorine solutions and obtained gluconic and 5-ketogluconic acids. Aqueous chlorination of methyl β-cellobioside at pH 1.0 yielded cellobionic acid initially with subsequent formation of gluconic acid (39). In neither case did comparable applications of hydrochloric acid alone yield similar transformations.

The methyl glucopyranoside was treated with aqueous chlorine at pH 4.5 by Henderson (40). In this instance, oxalic, 2-ketogluconic acid, and 2,5-diketogluconic acid were obtained as reaction products. Cotton was found to behave similarly.

These few references are typical of many similar studies. The results indicate that cleavage of the β-link in cellulose occurs. In addition, oxidation at other carbons in the glucose unit is seen to occur. Oxidation of this type may lead to further degradation if alkali is applied due to the so-called "peeling" reaction (37).

EXPERIMENTAL PROGRAM

The purpose of the experimental program was to investigate the influence of chlorine concentration, reaction pH, and reaction temperature on the aqueous chlorination of two kraft pulps. Reaction durations of less than one minute were employed. Changes in lignin and chlorine contents of the pulps were used to follow the course of the chlorination reactions. This information was supplemented by determinations of pulp viscosities after chlorination and chlorine consumption during chlorination.

CHLORINATION APPARATUS

In previous investigations, batch chlorinations were employed in which known quantities of pulp and chlorine were reacted in a sealed container. This approach is unsuitable when short reaction periods are required as the time involved in sampling the reaction medium may be quite large in comparison to the desired reaction time.

On the other hand, tubular flow reactors have been used widely to study fluid phase reactions of short duration. With appropriate modifications, this technique was adopted for use in the present investigation. In subsequent sections, the reactor is described along with factors affecting its operation and an evaluation of its reproducibility.

A flow diagram of the reactor system is shown in Fig. 6, and the actual system is presented in Fig. 7. Since the arrangement of the two feed systems was the same, only the chlorine lines and pump are labelled in Fig. 7.

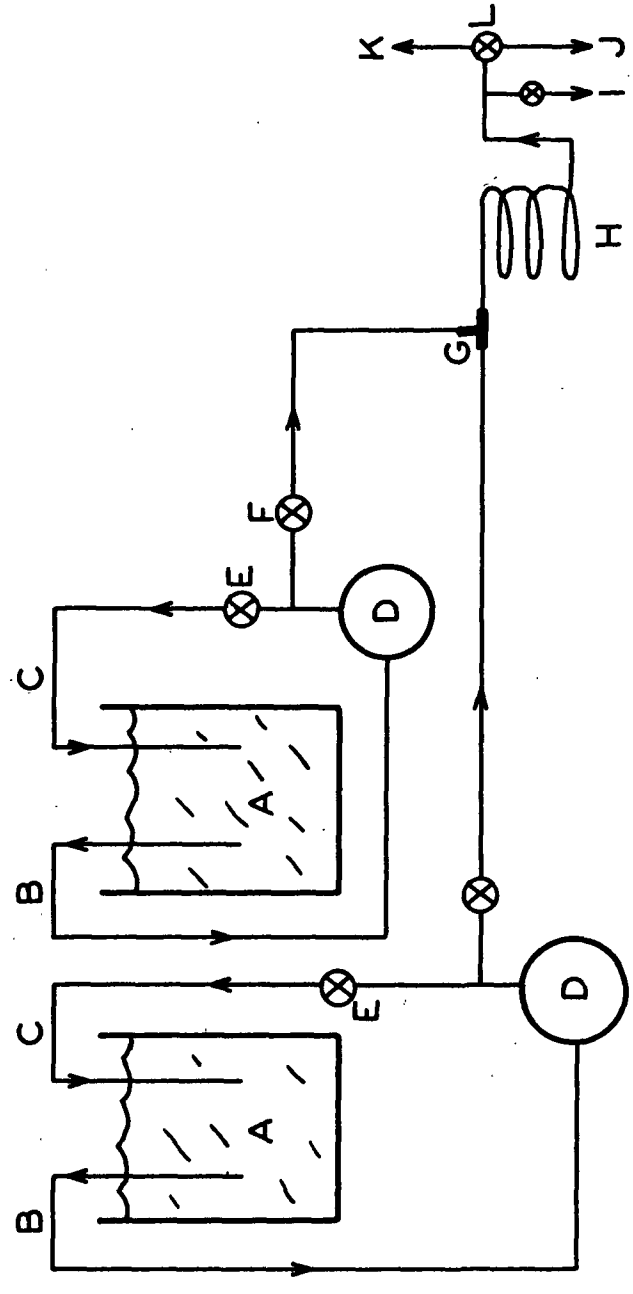
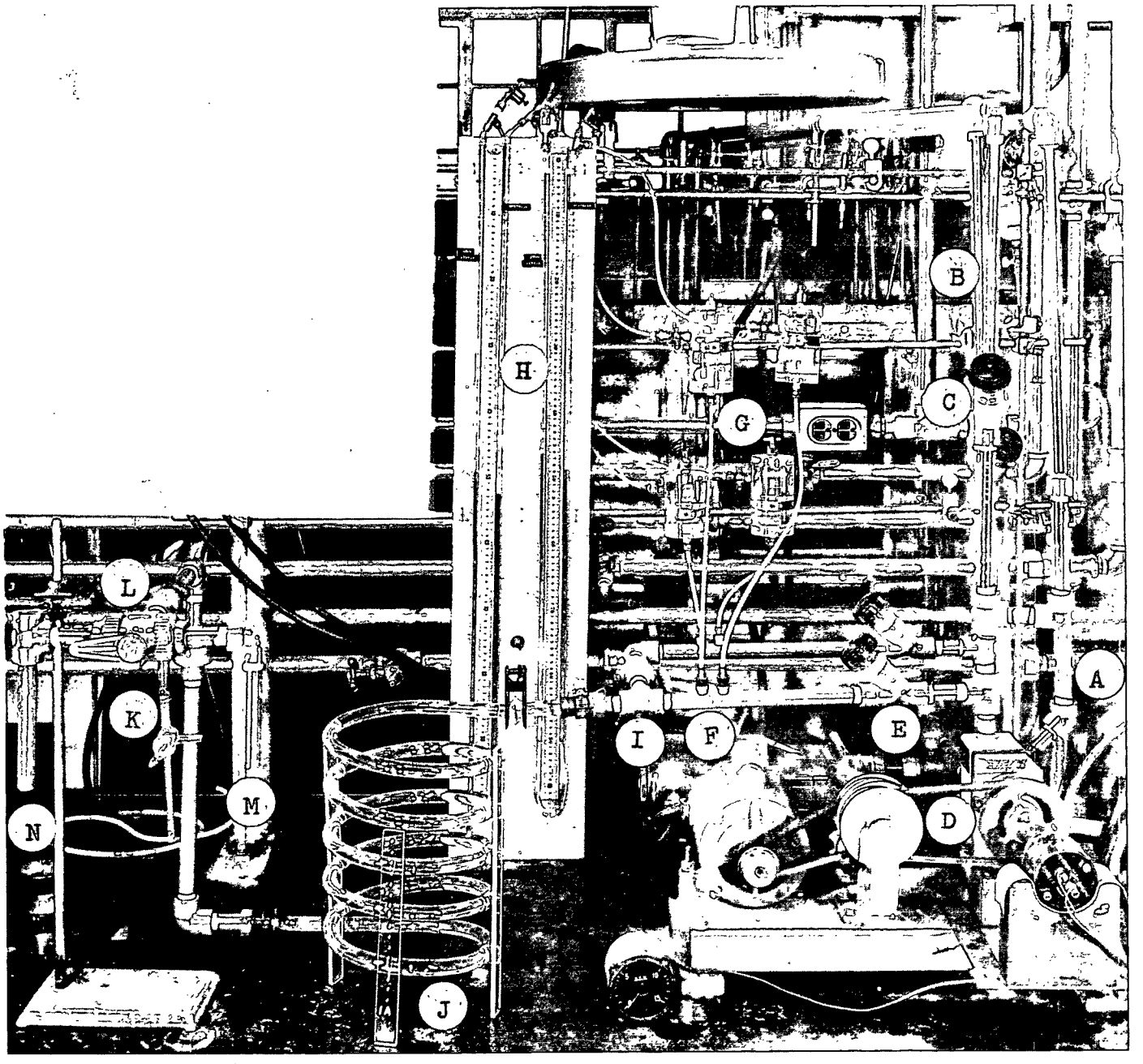


Figure 6. Reactor Flow Diagram



A — Intake Line
B — Bypass Line
C — Bypass Valve
D — Feed Pump
E — Feed Valve
F — Eccentric Orifice
G — Manometer Traps
H — Manometers
I — Mixing Tee
J — Reactor Coil
K — Liquor Sample Port
L — Discharge Valve
M — Pulp Sample Line
N — Sewer Line

Figure 7. Reactor System

The various parts of the reactor shown in this figure can be classified into three functional systems. Preparation and storage of the reactants, pulp meal suspensions, and aqueous chlorine solutions, were accomplished in the reservoir system. The feed system was used to supply the reactants at controlled rates to the mixing tee. A variable length reaction chamber system, including the tee, reactor coils, and connecting tubing, was employed in the control of the reaction duration. This latter system included the sampling ports needed to follow the course of the chlorination reactions.

The design of the reactor resulted from a consideration of many interdependent factors. The desired reaction time range was obtained by selecting the proper combination of feed rates and reaction chamber volumes. This choice, in turn, influenced the selection of pump capacities and the diameter of the reactor coils, feed lines, and connecting tubing. The desirability of attaining turbulence in the reaction chamber to promote mixing was considered here also.

The capacity of a reservoir was chosen to yield the maximum number of chlorination runs per reservoir charge and still remain small enough to permit good control of the conditions within the reservoir. This capacity was influenced by the volume of reaction stream required to collect samples of sufficient size to permit reliable analysis. A certain quantity of material had to be sewered while equilibrium was being established in the reaction chamber; therefore, a reservoir capacity had to provide this additional material.

Another important feature in the design of the reactor system was the ease of operation. To achieve this goal, the feed rate controls and sampling ports were positioned as close together as possible so the important operations of flow adjustment and sampling could be accomplished efficiently. Threaded pipes

were used in the construction so that inspection and cleaning of various reactor parts could be performed easily.

The corrosiveness of chlorine directed the selection of materials to be used and necessitated thorough flushing of the system after every set of chlorination runs.

In the following sections the reactor system is described in greater detail.

RESERVOIR SYSTEM

A diagram of the reservoir system is presented in Fig. 8. The actual system is shown in Fig. 9.

Cylindrical glass jars, each having a thirty-liter capacity, were used as reservoirs for the pulp suspensions and the chlorine solutions. Since the temperature of the reaction stream was governed by that of the reservoirs, they were placed in a thermostatically-controlled water bath which was adjusted to the desired reaction temperature.

Agitation was provided to insure uniform conditions within a reservoir. The action of the stirrers and recirculation of the feed streams during operation of the reactor system resulted in a 2 to 3°F. rise in the reservoirs. As a result, it was necessary to standardize the durations of both stirring and recirculation for all runs.

The liquid level within a reservoir fell continuously during a run; therefore, neither reservoir was sealed. This arrangement necessitated the installation of a hood over the chlorine reservoir to avoid contamination of the bath water, corrosion of metal parts, and any health hazard. Chlorine losses to the atmosphere were found to be minor except with the use of a

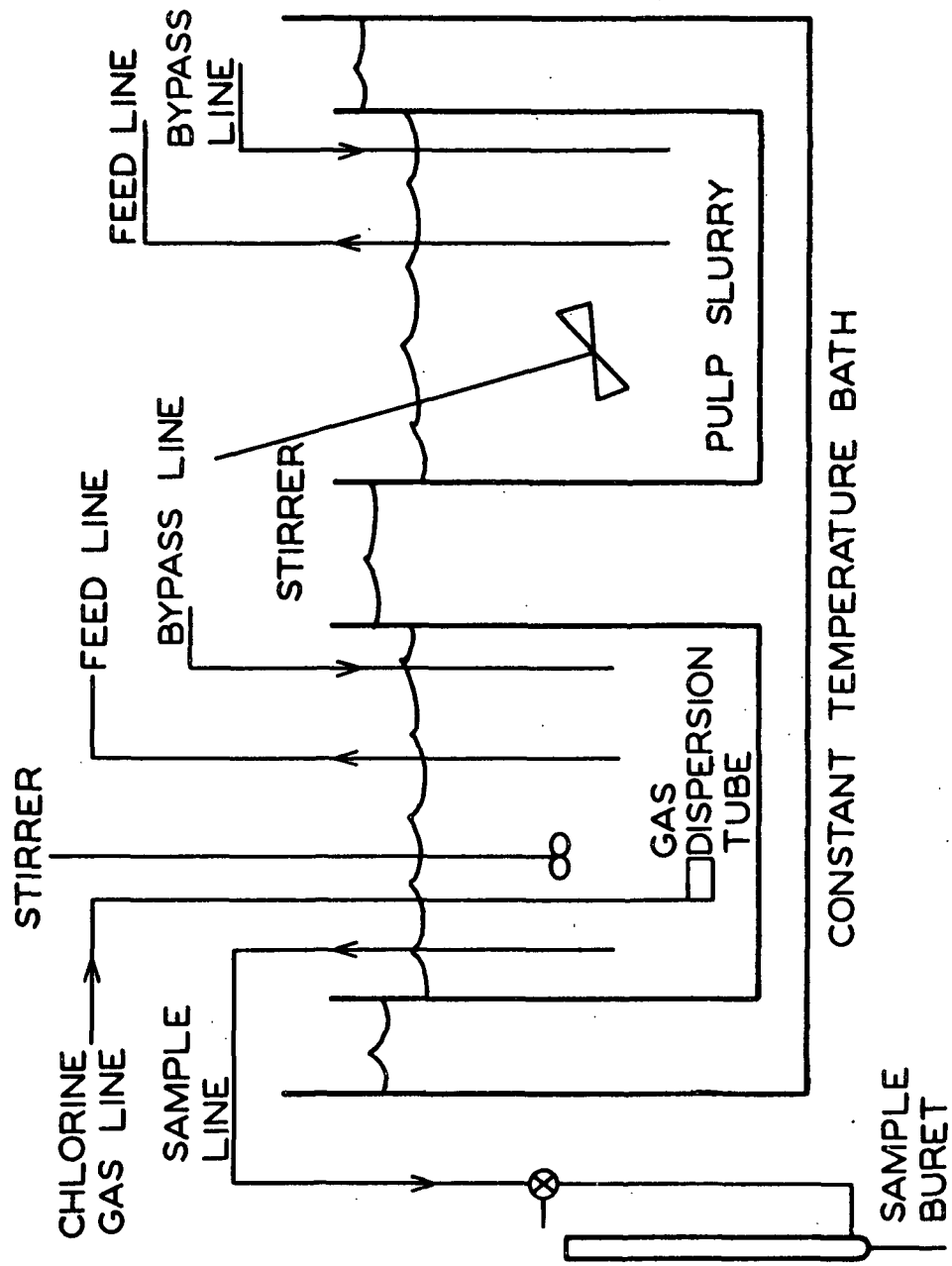
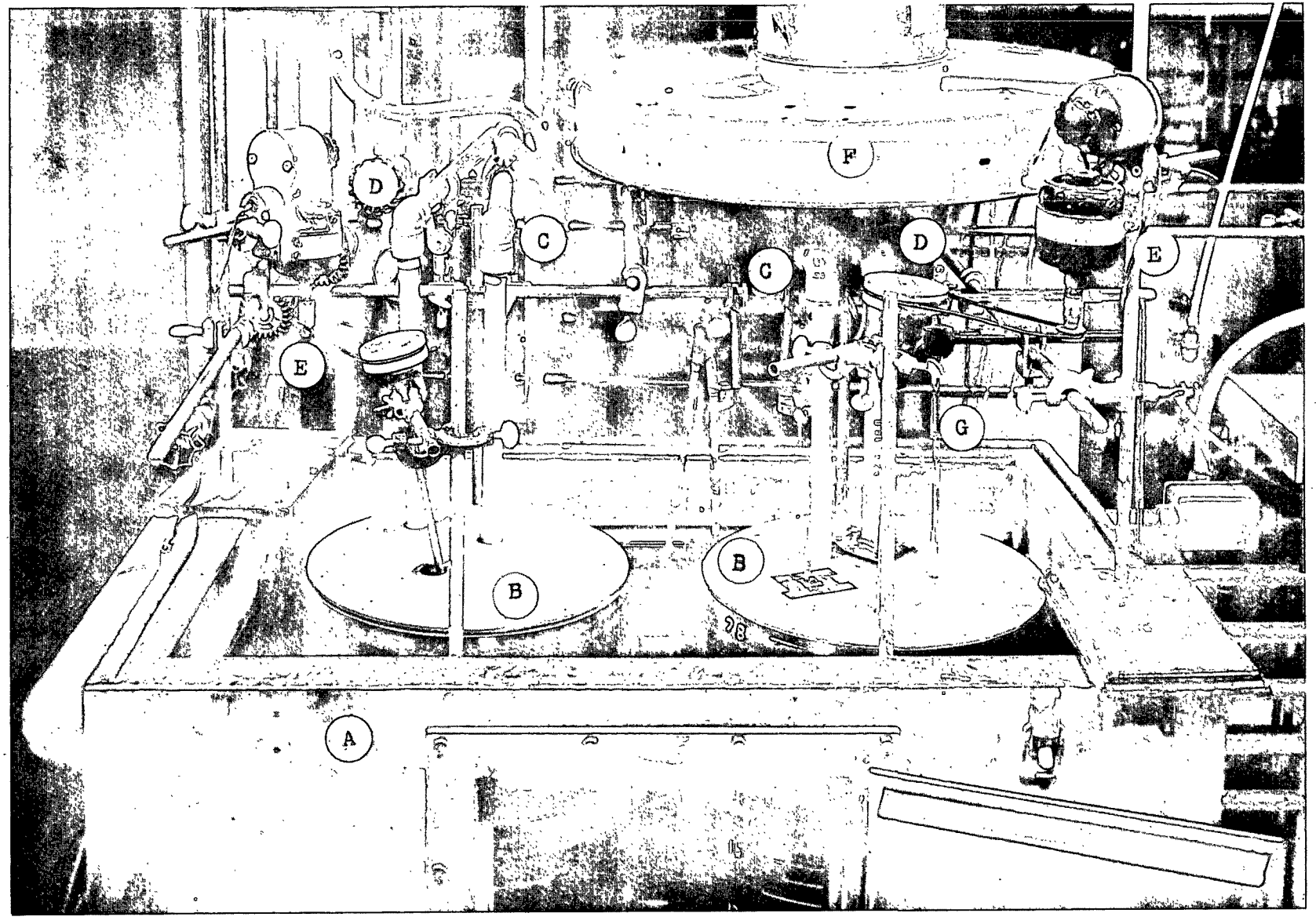


Figure 8. Reservoir System



A — Constant Temperature Bath
B — Reservoir D — Bypass Lines F — Hood
C — Intake Lines E — Stirrers G — Liquor Sample Line

Figure 9. Reservoir System

solution pH lower than two. In these chlorination experiments, it was necessary to restore the concentration in the reservoir to the desired value prior to each run.

Chlorine solutions were prepared by bubbling gas through a dispersion tube immersed in distilled water. Adjustments in the pH of a chlorine solution were made by additions of concentrated hydrochloric acid or sodium hydroxide. Samples were withdrawn from the chlorine reservoir through the sample line shown in Fig. 8. Since only the lower half of a chlorine sample in the sampling buret was analyzed, no loss of chlorine from the sample should have occurred.

The pulp slurry was prepared by adding sufficient fiber to a known volume of distilled water to yield the desired consistency. The fibers in a measured volume of the pulp suspension were collected and weighed in a fritted glass filter crucible in the consistency determination.

Since a reservoir was emptied during a chlorination trial, buoyant forces tended to tip it over. Harnesses and guide rods were installed to minimize all but vertical movement. This arrangement is shown in Fig. 10.

In addition, the flow rate of a feed pump was found to be dependent on the liquid height over the intake line. The upward movement of a reservoir partially offset the decreasing liquid level. The net result was a more stable flow rate.

FEED SYSTEM

The feed system was the most important component of the flow reactor as it determined the reaction time for a given reaction chamber volume, and it controlled both the initial conditions in the reaction stream and the mixing of pulp and chlorine throughout the reaction chamber.

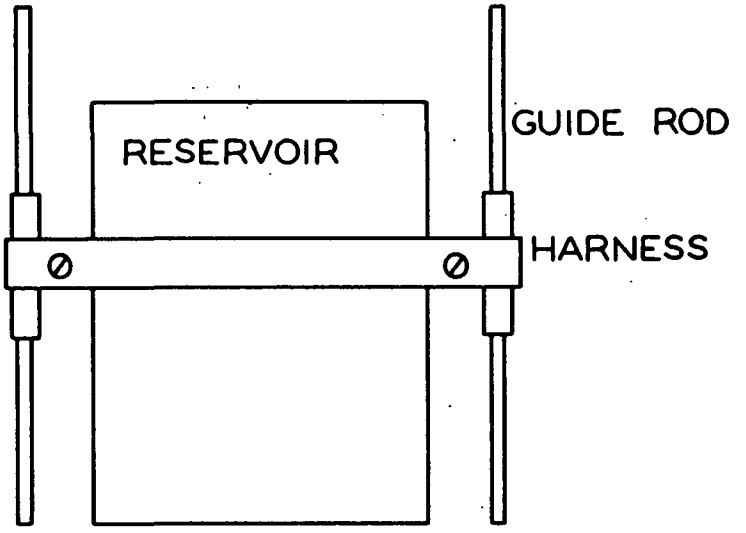


Figure 10. Reservoir Guide System

The pulp feed pump was a Jabsco Model JC-1/2 inch equipped with a Zeromax Model JM speed regulator. This pump exhibited a pulse-free flow which was nearly independent of back pressure variations.

A Vanton pump, Model XB-T18, supplied aqueous chlorine to the reaction chamber. A variable-pitch pulley drive and a valve in the discharge line were used to regulate the flow rate. Flow pulsations, resulting from the action of the Vanton pump, were eliminated by an air cushion in the discharge line. The pump parts in contact with chlorine were a Teflon body block and a Hypalon flexi-liner. After repeated exposure to chlorine, a flexi-liner would fail and replacement was necessary.

The feed and bypass lines were 1/2-inch I.D., schedule 80 polyvinyl chloride pipe. Polyvinyl chloride valves and fittings were used also. Threaded joints, sealed with Teflon tape, were employed to assemble the system.

Bypass lines in the feed system permitted the attainment of an equilibrium in intake lines and pumps prior to combining the two feeds. This stabilization period was necessary particularly in the chlorine system as the Vanton pump speed exhibited a tendency to drift just after starting.

An eccentric orifice was used in the measure of each of the two feed rates. The details of an orifice are shown in Fig. 11. Traps were included to minimize the entry of either fibers or chlorine into the manometers. Carbon tetrachloride and monochlorobenzene were used in the chlorine feed and pulp feed manometers, respectively. Both fluids were dyed with Dupont Oil Red to accentuate the heights of these fluids in the manometers.

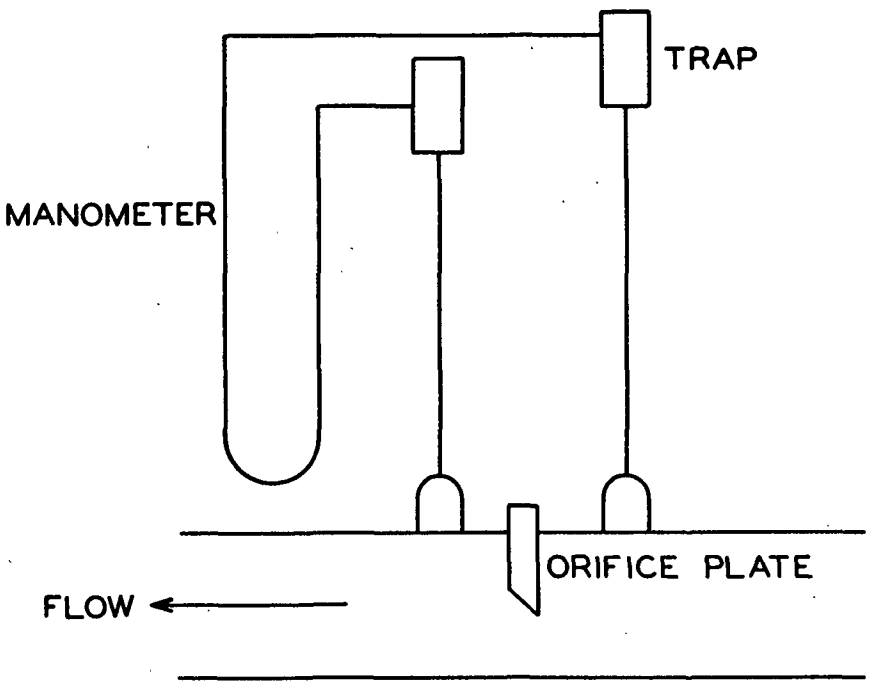


Figure 11. Eccentric Orifice

Each pump was calibrated by noting the level difference in the appropriate manometer while collecting a flow sample at the reactor discharge. The calibration curves were rechecked periodically throughout the study. After every calibration check, the combined flow rates estimated from manometer readings were compared with measured rates. The results of one of these comparisons are shown in Table II. In similar comparisons, average deviations of 1.89, 3.65, and 0.99% were obtained. Generally, a maximum deviation of 4% was found in these comparisons. It is believed that the small uncertainty in the flow control did not affect the usefulness of the reactor system.

TABLE II

COMPARISON OF CALIBRATED AND MEASURED FLOW RATES

Combined Flow Rate, cc./sec.		Deviation $\left(\frac{M-C}{M} \times 100\right)^a$, %
Calibrated (C)	Measured (M)	
62.8	61.4	2.28
67.3	64.9	3.70
66.9	65.5	1.50
63.8	63.8	0.0
65.3	65.1	0.31
67.4	65.2	3.37
68.3	67.4	1.34
57.5	56.4	1.95
56.8	58.4	2.74
65.0	61.7	5.35
	Av.	2.26

[a] Absolute values.

Estimated consistencies, calculated from relative feed rates and the reservoir consistency, were compared with measured consistencies. Average deviations for three combined flow calibrations were 2.48, 2.17, and 1.29%. Here again, the maximum deviation generally remained below 4%. A tendency for the measured value to be higher than the estimated value was observed.

REACTION CHAMBER

The chlorination of a pulp began at the mixing tee and continued until the chlorine was quenched at the reactor discharge.

In nearly all runs, a constant flow rate was employed; and the reaction time was varied by changes in the reaction chamber volume. These changes were achieved by the use of glass coils placed in series. The coils were constructed of 1/2-inch I.D., heavy wall, glass tubing fitted with ball and socket joints. Spring-loaded metal clamps held the joints together firmly. The capacities of the coils and other reaction chamber lines were determined by measuring the volume of water contained in each part. The seven reaction chamber volumes employed in this study are listed in Table III; the designation 0 – 6 indicates the number of coils in series with connecting tubing.

TABLE III

REACTION CHAMBER VOLUMES

No. of Coils	Reactor Volume, cc.
0	240.4
1	649.2
2	987.9
3	1399.3
4	1741.2
5	2151.2
6	2495.3

The deviation found in the flow-rate control obviously introduced some uncertainty in the definition of the reaction time. The determination of volumes of connecting tubing was another possible source of error in this definition. The latter uncertainty would be of greater importance at shorter reaction times; however, any error from the volume measurements was common to all experiments.

In flow systems, definition of reaction time can be affected also by inadequate mixing at the initiation of the reaction. This initial mixing included another factor in the present study. The aqueous chlorine feed was diluted in the mixing tee which, through further hydrolysis, should have caused shifts in the relative amounts of molecular chlorine and hypochlorous acid. The rapidity of this hydrolysis, as reported in the literature, indicated that this initial readjustment occurred almost instantaneously in comparison with the total reaction times (14-15).

Continued, intimate contact between reactants throughout the reaction chamber is required. In the present system, this requirement was influenced by the presence of fibers. It is known that pulp suspensions flowing through circular pipes at moderate velocities form a fiber "plug" surrounded by a "clear water annulus" (41-44). This fiber network would minimize mixing of various parts of a flow stream. As a result, localized depletions of chlorine, due to the rapidity of chlorination in its early phase, might occur if a fiber plug existed in the reaction chamber.

The formation of a fiber network depends on fiber length and pulp consistency. A flow tube which permitted the injection of a dye into the flow stream was constructed to obtain an estimation of the effects of these two factors on turbulence. On the basis of this preliminary work, a reaction stream consistency of 0.1% was selected and the fibers to be used in the chlorination

runs were ground in a Wiley mill. Grinding probably altered the fibers somewhat so that their response to chlorination may not be exactly the same as the whole fibers. The viscosity of the whole pulp was reduced by only 1.3% during grinding so it is believed that no drastic changes occurred. As a result, the chlorination of the pulp meal should not differ greatly from the whole fibers. In addition, it is believed that the use of different woods and chlorinating systems may be as important as the physical form of the fibers in comparisons of the results of the present study with those obtained in other investigations of pulp chlorination.

Samples for residual chlorine concentration determinations were removed from the reaction chamber by the delivery line shown in Fig. 12. The glass wool filtered fibers from the liquor sample. Periodic inspection indicated no accumulation of pulp on the glass wool occurred. The usefulness of this sampling set-up was tested by comparing the chlorine reservoir concentration with that measured at the sampling port when only chlorine water was pumped through the system. The results of three separate comparisons are shown in Table IV. The agreement was good.

TABLE IV

COMPARISON OF RESERVOIR AND REACTOR DISCHARGE CHLORINE CONCENTRATIONS

Test No.	Chlorine Concentration, g./l. Reservoir	Reactor Discharge
1	1.525	1.531
2	1.533	1.527
3	1.515	1.524

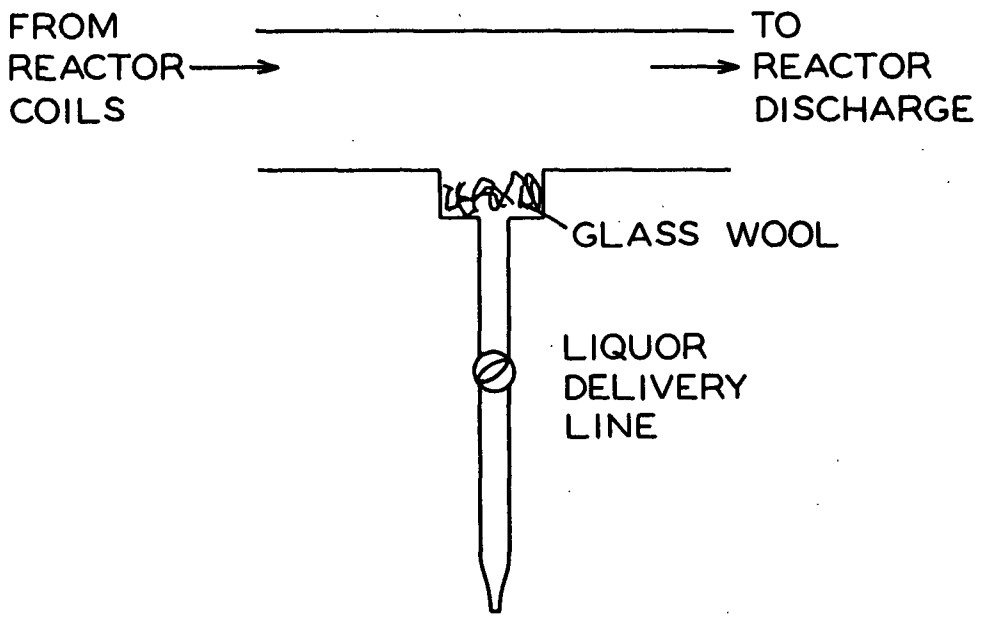


Figure 12. Liquor Sampling Port

Residual chlorine concentrations were determined also in four blank trials in which no fibers were present. A reaction stream concentration was estimated from the relative flow rates of the two feeds. This value was compared with a concentration measured at the reactor discharge. Deviations for the four trials were 5.1, 1.7, 1.6, and 1.8%, with an average of 2.4%. The variations were random and about the same as that encountered in estimations of total flow and reaction stream consistency. This degree of uncertainty limited the usefulness of consumption values in the interpretation of the results.

Pulp samples were obtained by directing the reaction stream into a 5% sodium metabisulfite solution. Vigorous agitation was applied during quenching to augment rapid and complete cessation of the chlorination reaction. Efficient quenching was promoted also by using the reagent in excess of over 100% of that required to reduce the residual chlorine. Inadequate quenching would introduce an error into the definition of reaction time.

The liquor sampling port and the point of pulp sample collection were separated by a length of tubing; therefore, the two samples did not correspond to a single reaction time. This factor was considered when chlorine consumption was compared with the extent of pulp reaction.

A sample of the unquenched reaction stream was collected for measurement of pH and temperature. This sample should have reflected the reaction temperature quite well; however, the pH value was affected by the production of acid by the chlorination reaction. Since small quantities of fiber were present in a unit volume of reaction stream, acid concentration changes due to reaction were believed to be minor. In addition, no trend toward increased acidity as the reaction duration increased was observed. Therefore, the measured values were used to represent the reaction pH.

OPERATION OF THE REACTOR SYSTEM

The procedure for any one trial is described here in chronological order:

(1) Both reservoirs were filled with distilled water and were conditioned to the desired reaction temperature in the water bath.

(2) Pulp consistency and chlorine concentration values were brought to the proper levels.

(3) The reaction chamber volume was adjusted.

(4) The two feed pumps were started, and the feed streams were recirculated for ten minutes.

(5) The discharge valve was set to direct the reaction stream to the sewer.

(6) Next, the feed streams were directed to the reaction chamber, and their flow rates were adjusted.

(7) The reaction stream was pumped to the sewer for a period equal to 1-1/2 times the desired reaction period to permit stabilization of the flow in the reaction chamber.

(8) A sample of the reaction stream was collected in the quench tank. Constant adjustment of the feed rates was performed during quenching. Next a sample of the unquenched reaction stream was collected, and its temperature and pH were measured.

(9) The reaction stream was redirected to the sewer, and a liquor sample was collected. It was not possible to correct any flow variations which occurred during this sampling period.

(10) The feed streams were recirculated once again prior to stopping the feed pumps.

(11) The liquor sample was analyzed for chlorine.

(12) The chlorinated pulp was filtered and washed free of the quenched reaction solution.

(13) The system was then readied for the next run. Three or four runs could be performed before the reservoir charges were depleted.

(14) A chlorinated pulp sample was divided into two portions. One portion was set aside for determination of organically-bound chlorine. The other was extracted with alkali. The extracted samples were used in the Klason lignin and pulp viscosity tests.

REPRODUCIBILITY OF THE REACTOR SYSTEM

Possible sources of error in the use of the reactor system have been noted. The usefulness of the data obtained in this study depended on how serious these errors were. As a test of the reproducibility of the system, a number of duplicate chlorination trials were performed; the results are presented in Table V.

TABLE V

DUPLICATE CHLORINATION TRIALS

Sample	Reaction Temp., °F.	Reaction pH	Chlorine Concn., g./l.	Reaction Time, sec.	Klason Lignin, %[a]
1D	70.0	--	1.28	16.5	1.69
2D	70.0	--	1.28	16.5	1.64
MD2	72.4	3.14	0.79	10.8	5.62
A1	72.4	3.18	0.78	10.8	5.76
M1	72.0	3.14	0.79	34.9	4.64
M2	72.0	--	0.77	34.6	4.59
MD	72.0	3.21	0.78	35.8	4.82
A5	72.4	3.18	0.78	35.8	4.67

[a]Based on original pulp.

The average difference between lignin content pairs is about 0.1%. This comparison indicated that the reproducibility of the reactor system was not affected at shorter reaction times. The chlorinations of Samples M1, M2, and MD were performed under very similar conditions. The flow rates of the reaction stream were 48.5, 60.0, and 72.3 cc./sec. for M1, MD, and M2, respectively. The lignin values of these samples showed no dependence on flow rate; therefore, mixing errors apparently were minor in the reactor system.

In view of the many potential sources of error, the observed reproducibility was accepted as being quite good.

EXPERIMENTAL TECHNIQUES

PULP PREPARATION

Two spruce kraft pulps were employed in this study. The digestion conditions are listed in Table VI.

TABLE VI

PREPARATION OF KRAFT PULPS

	PU1	PU2
Max. temp., °C.	176	176
Time to temp., min.	97	90
Time at temp., min.	25	20
NaOH (as Na_2O), %[a]	13.5	13.3
Na_2S (as Na_2O), %[a]	4.5	4.5
Klason lignin content, %[b]	7.24	9.88

[a] Basis, moisture-free wood.

[b] Basis, moisture-free pulp.

After washing and screening, the pulp designated PU1 was centrifuged and shredded. The pulp crumbs were placed in polyethylene bags and were stored in a cold room. The other pulp (PU2) was prepared by the Pulping Group of the Technology Section and was received in airdry form.

Both pulps were fractionated in a Bauer-McNett classifier. The material passing a 65-mesh screen was rejected. The acceptable pulp was centrifuged, shredded, and air dried.

Pulp grinding was accomplished in a Wiley mill fitted with a screen having a hole diameter of 0.076 inch. Unground cores of the air-dried pulps and fine fiber fragments were removed by screening with Tyler Standard Screens mounted in a sieve shaker. The fibrous material passing a 170-mesh screen and that retained by a 30-mesh screen were rejected.

ALKALINE EXTRACTION

Prior to lignin and viscosity measurements, pulp samples were extracted with sodium hydroxide at 2% consistency and 60°C., for one hour. The hydroxide application was 10% based on the airdry pulp weight. This basis was acceptable since the moisture contents of the airdry samples were quite uniform. The extraction suspension was stirred frequently.

ANALYSES

Chlorine Concentration

Samples of aqueous chlorine solutions were analyzed according to TAPPI Standard Method T-611. This iodometric titration yields "available" chlorine values, that is, the sum of the molecular chlorine and hypochlorous acid present.

Organically-Bound Chlorine

The chlorine content of a pulp was utilized as a measure of chlorine substitution into the lignin. Samples of the unextracted pulps were compressed in a Parr Pellet press. These pellets were dried overnight under vacuum at 60°C. Drying at higher temperatures led to discoloration of the samples.

The pulp pellets were burned in a Thomas-Schoniger combustion flask. Combustion products were absorbed by an alkaline solution over a thirty-minute period. The chloride solution was then boiled for 3 to 5 minutes, then acidified and boiled for an additional 2 minutes (45).

The acidic solutions were diluted to 100 ml. in volumetric flasks. Chloride determinations were performed using Technicon's Autoanalyzer. In this test, chloride solutions were mixed with ferric alum sulfate, 6% by weight in 6N nitric acid, and a saturated solution of mercuric thiocyanate. The ferric thiocyanate complex formed in this system is directly proportional to the chloride concentration and was determined colorimetrically at a wavelength of 480 mμ. The absorbance of a sample was related to chloride concentration by means of a calibration curve based on sodium chloride solutions of known concentrations (46).

The presence of inorganic chloride in the pulp was undesirable. Therefore, a sample of untreated pulp was slurried in a 0.01M hydrochloric acid solution. This sample was washed by the same procedure applied to chlorinated pulps. Analysis of the sample showed no chloride was present. The washing technique effectively removed inorganic chloride from the pulp.

It is known that chlorinated lignin is water soluble to a degree determined by the chlorination conditions (11,12,22,27). The literature indicates that time and temperature are the important factors in the solubilization of chlorinated lignin in the absence of alkali. In order to minimize such losses, chlorinated pulps were washed with water which had been cooled to 8°C. The sodium metabisulfite solution was cooled similarly so that the temperature of the quenched reaction stream did not exceed 19°C. in any of the trials. The time of contact between the chlorinated pulp and the quenched reaction solution was never more than eight to ten minutes. Under these conditions, losses of

chlorinated lignin should have been minor. Sarkanen and Dence (28) and Loras (47) employed the absorbance of isolated lignins in the ultraviolet light region in their studies. This technique was applied to filtrates obtained from chlorination trials in which delignification was extensive. No absorbance peaks were observed. It was assumed then that the losses of chlorinated lignin were minor.

Klason Lignin

The Klason lignin content of a pulp sample was determined according to TAPPI Standard Method T 222 M-43. Although the term "lignin content" is used throughout this report, the values actually represent the acid-insoluble residue obtained from the hydrolysis of pulp carbohydrates with 72% sulfuric acid.

Generally, lignin contents are corrected with yield values which account for carbohydrate and lignin losses from the original pulp. In the reactor system, it was not possible to determine yield values directly; instead they were calculated from the quantity of reaction stream collected in a trial, pulp reservoir consistency, and relative flow rates of the two feeds. The deviation between estimated and measured consistencies reported earlier influenced the yield calculations. As a result, no trend in yields was observed over the reaction period. Average yield correction for a set of chlorination conditions would alter a lignin-time plot uniformly over the reaction duration. On the other hand, true yield corrections would become increasingly larger as the reaction time increased.

The thesis work of Chapnerkar (12) was examined to estimate carbohydrate losses during aqueous chlorination of a kraft pulp. Using his data, yield values were calculated, assuming only lignin removal. These calculated values are compared in Table VII with those determined experimentally by Chapnerkar. This comparison indicated little carbohydrate loss occurred even when extensive

delignification was obtained. Therefore, it was assumed carbohydrate loss was minor, and yield values were calculated assuming only lignin removal. In most instances calculated yield values differed from experimental values obtained with the flow system by 2 to 4%.

TABLE VII

A COMPARISON OF MEASURED AND CALCULATED YIELDS

Reaction[a] Time, min.	Reaction[a] Temp., °F.	Chlorine[a] Concn., g./l.	Original[a] Lignin Remaining, %	Measured[a] Yield, %	Calculated[b] Yield, %
5	87	0.57	27.5	92.0	92.0
	66	0.57	39.1	92.3	93.3
	77	0.57	30.1	92.6	92.3
	77	0.90	23.6	91.5	91.5
	77	1.63	14.4	90.1	90.3
30	77	0.57	11.3	89.4	89.9
	77	0.90	9.8	88.7	89.8
	77	1.63	9.3	88.5	89.7

[a] Reported by Chapnerkar (12).

[b] Calculated from Chapnerkar's data.

Pulp Viscosity

Samples intended for viscosity determinations were treated with sodium chlorite to remove most of the residual lignin. This treatment involved applications of 50% acetic acid and 10% sodium chlorite, based on the pulp weight. The samples were chlorited at 2% consistency and 65°C. for thirty minutes.

The delignified samples were analyzed for viscosity according to TAPPI Standard Method T 230-su-63.

EXPERIMENTAL DATA

The data obtained in the chlorination runs are presented in Table VIII. The reaction conditions for a series of experiments are averages for the seven reaction times involved. As stated previously, the reaction pH and temperature were measured at the reactor discharge; and the initial chlorine concentration and consistency values were calculated from relative flow rates of the two feeds and conditions in the reservoirs. Lignin contents are expressed as a per cent of the original pulp and were corrected by yield values calculated on the basis of only lignin removal from a pulp during chlorination. Bound chlorine contents are based on the vacuum-dry weight of the chlorinated pulp after correction for the chloride present.

The designation 0 to 6 corresponds to the seven reactor volumes presented in Table III. To avoid repetition, the seven reaction times used in the runs are shown here:

Sample Designation	Reaction Time, sec.
0	4.0
1	10.8
2	16.5
3	23.3
4	29.0
5	35.8
6	41.6

Constant adjustment of the reaction stream flow rate was made during pulp sampling; therefore, these seven times could be duplicated, within the limits of the control system, for each set of chlorination conditions. Both hands of the operator were needed in the liquor sample collection. As a result, any flow rate variations could not be corrected; therefore, manometer readings taken during sampling were used to calculate the reaction time for each sample. Total chlorine consumption values are shown in Table IX with their respective reaction times.

TABLE VIII

CHLORINATION DATA

Sample Identification	pH	Temp., °C.	Consist., g./l.	Chlorine Concn., g./l.	Klason Lignin Content, % original pulp	Chlorine Content, mole chlorine$_5$/ g. pulp x 10^{-5}	Pulp Viscosity, cp.
PU1	--	--	--	--	7.24	0.0	21.0
E0	3.75	21.5	1.04	0.81	6.70	--	21.2
E1					6.64	--	--
E2					6.68	--	20.1
E3					6.65	--	--
E4					6.57	--	18.2
E5					6.68	--	--
E6					6.52	--	18.6
D0	3.55	21.4	1.05	1.01	6.56	1.2	--
D1					6.34	3.9	--
D2					6.55	2.5	--
D3					6.47	4.3	--
D4					6.47	4.3	--
D5					6.52	3.8	--
D6					6.38	4.0	--
F0	3.68	21.1	1.03	1.31	6.43	--	--
F1					6.30	--	--
F2					6.21	--	--
F3					6.33	--	--
F4					6.33	--	--
F5					6.24	--	--
F6					6.11	--	--
H0	4.03	8.8	1.03	1.03	6.85	--	--
H1					6.81	--	--
H2					6.84	--	--
H3					6.75	--	--
H4					6.64	--	--
H5					6.27	--	--
H6					6.15	--	--

CHLORINATION DATA

Sample Identification	pH	Temp., °C.	Consist., g./l.	Chlorine Concn., g./l.	Klason Lignin Content, % original pulp	Chlorine Content, mole chlorine$_5$/ g. pulp x 10^{-5}	Pulp Viscosity, cp.
B0	3.02	22.7	1.03	0.52	7.05	3.1	--
B1					6.74	4.5	--
B2					6.79	7.6	--
B3					6.31	8.6	--
B4					6.23	11.1	--
B5					5.53	16.1	--
B6					5.42	17.0	--
A0	3.18	22.7	1.04	0.78	6.64	5.1	18.3
A1					5.92	8.6	--
A2					5.43	11.0	15.6
A3					5.08	12.5	--
A4					4.49	17.5	19.3
A5					4.67	24.1	--
A6					4.13	25.9	17.8
C0	3.02	22.7	1.02	1.07	5.77	12.7	17.3
C1					4.85	16.9	--
C2					4.19	24.2	--
C3					3.72	24.7	15.0
C4					3.48	29.0	--
C5					2.94	29.3	--
C6					2.59	25.4	17.3
S0	3.10	16.1	1.03	0.77	6.17	5.2	--
S1					6.26	10.9	--
S2					5.91	12.1	--
S3					5.04	19.7	--
S4					5.00	20.4	--
S5					4.60	19.4	--
S6					4.60	22.0	--
V0	3.05	14.0	1.03	1.06	5.39	15.3	18.6
V1					5.55	14.3	--
V2					5.13	17.7	--
V3					4.95	17.9	18.7
V4					4.30	25.9	--
V5					4.05	26.3	15.6
V6					3.60	26.7	--

TABLE VIII (Continued)

CHLORINATION DATA

Sample Identification	pH	Temp., °C.	Consist., g./l.	Chlorine Concn., g./l.	Klason Lignin Content, % original pulp	Chlorine Content, mole chlorine / g. pulp x 10^{-5}	Pulp Viscosity, cp.
J0	2.97	8.7	1.02	0.78	6.16	7.5	--
J1					5.62	10.1	22.7
J2					5.18	14.4	--
J3					5.06	14.4	24.1
J4					4.73	14.7	--
J5					4.16	21.3	24.7
J6					4.15	21.2	--
P0	1.32	22.3	1.04	0.76	2.53	36.8	--
P1					2.39	35.1	8.3
P2					1.86	37.4	--
P3					1.52	40.7	8.3
P4					1.44	42.0	8.8
P5					1.07	39.6	--
P6					1.40	35.4	--
PU2	--	--	--	--	9.88	0.0	--
L0	3.96	20.8	1.03	1.28	9.25	--	--
L1					8.88	--	--
L2					8.58	--	--
L3					8.65	--	--
L4					8.42	--	--
L5					8.17	--	--
L6					7.84	--	--
N0	3.05	21.5	1.03	1.07	7.99	11.7	--
N1					6.96	16.4	--
N2					6.12	22.1	--
N3					5.74	25.2	--
N4					4.10	35.7	--
N5					4.05	36.6	--
N6					3.61	38.5	--

TABLE IX

TOTAL CHLORINE CONSUMPTION

Sample	Reaction Time, sec.	Consumption, % applied chlorine	Sample	Reaction Time, sec.	Consumption, % applied chlorine	Sample	Reaction Time, sec.	Consumption, % applied chlorine
E0	--	--	A0	3.6	95.3	L0	--	--
E1	10.4	98.4	A1	10.5	97.0	L1	--	--
E2	16.5	100.0	A2	15.7	98.5	L2	16.3	101.5
E3	23.0	100.2	A3	22.9	97.8	L3	--	--
E4	--	--	A4	29.1	91.3	L4	--	--
E5	35.9	98.4	A5	35.6	99.3	L5	35.5	99.2
E6	41.4	96.5	A6	40.6	94.5	L6	41.4	96.3
D0	--	--	C0	3.6	97.8	N0	3.6	100.0
D1	10.6	106.7	C1	10.5	95.5	N1	10.3	98.3
D2	16.0	102.0	C2	16.3	94.5	N2	16.1	96.5
D3	--	--	C3	--	--	N3	23.2	98.6
D4	28.5	105.0	C4	28.6	95.3	N4	28.9	98.0
D5	35.5	95.8	C5	36.1	96.8	N5	35.5	94.4
D6	41.3	95.3	C6	41.5	92.5	N6	41.5	94.3
F0	--	--	S0	3.6	94.8	V0	--	--
F1	--	--	S1	10.3	102.0	V1	--	--
F2	16.0	99.5	S2	--	--	V2	16.2	101.0
F3	22.8	99.4	S3	28.8	100.0	V3	23.3	98.2
F4	28.5	106.0	S4	--	--	V4	28.8	99.0
F5	35.5	95.8	S5	--	--	V5	35.5	99.0
F6	41.3	97.8	S6	--	--	V6	41.9	97.5
H0	--	--	J0	--	--			
H1	10.9	97.0	J1	10.5	101.5			
H2	16.6	106.8	J2	16.7	102.8			
H3	23.0	96.5	J3	23.1	96.3			
H4	--	--	J4	28.6	105.8			
H5	25.5	101.5	J5	35.5	93.8			
H6	--	--	J6	41.3	96.8			
B0	3.7	90.0	P0	3.5	92.0			
B1	10.5	92.3	P1	10.5	83.8			
B2	15.7	--	P2	16.1	89.2			
B3	23.0	94.5	P3	22.6	88.0			
B4	28.7	94.5	P4	28.8	89.1			
B5	36.0	96.5	P5	35.6	87.8			
B6	--	--	P6	41.2	90.5			

RESULTS AND DISCUSSION

The effects of chlorine concentration, pH, and temperature on pulp delignification have received considerable attention in past studies involving relatively long chlorination periods. The results of the present study were used to estimate the influence of each of these variables during relatively short reaction durations. Any significant differences or similarities between the influence of a variable in the initial phase and in later reaction stages were examined. In so far as possible, the experimental data were employed also in an analysis of the nature of the delignification reactions. Unless otherwise noted, the following results were obtained from chlorination of PU1.

CHLORINE CONCENTRATION VARIATIONS

With few exceptions, the rate of a reaction is some function of the reactants' concentrations. In the present case, this relationship may be expressed as follows:

$$-dL/dt = k\, f\,(L,C) \qquad (1)$$

where: t = reaction time

C = chlorine concentration

k = rate constant

L = lignin concentration

A basic flaw in this type of expression is the inability to define accurately the lignin concentration. Regardless, rate equations having this general form have been applied in kinetic studies of both pulping and bleaching. In the latter case, the presence of two chlorine species in aqueous chlorine solutions must be considered in the chlorine concentration term.

Equation (1) may be simplified somewhat by applying chlorine in excess so that its concentration is essentially constant.

$$-dL/dt = k' f'(L) \quad (2)$$

$$k' = k f''(C) \quad (3)$$

where $\underline{k}'$ = pseudo rate constant.

Pulp chlorination studies have indicated that hypochlorous acid and molecular chlorine degrade lignin by different mechanisms. Appropriate adjustment of the reaction pH can be used to minimize the presence of molecular chlorine so that the action of hypochlorous acid may be examined separately. In this case, $\underline{C}$ in Equation (3) is defined as the hypochlorous acid concentration.

Three chlorination series were performed at concentrations of 0.81, 1.01, and 1.31 g./l.; the reaction pH was maintained between 3.55 and 3.75 to minimize the presence of molecular chlorine. In this pH region, the percentage of molecular chlorine in a solution is nearly independent of small changes in acidity. The results of these runs are shown graphically in Fig. 13. Only minor delignification was observed in these runs. The initial drop in lignin content may have resulted from reaction of easily oxidized material or an extraction of a lignin component. Increased applications of chlorine had no effect other than to increase the quantity of material removed initially.

No direct information was available as to the response of a kraft pulp to chlorination in this pH range in later reaction stages. However, Giertz (11) chlorinated an "artificial silk" pulp for periods ranging from three minutes to several hours at pH 3.9. He found lignin removal was greatly reduced as compared to chlorination at pH 1.0. A sulfite pulp and a kraft pulp were reported to behave similarly but no data were presented for the chlorination of the latter two pulps.

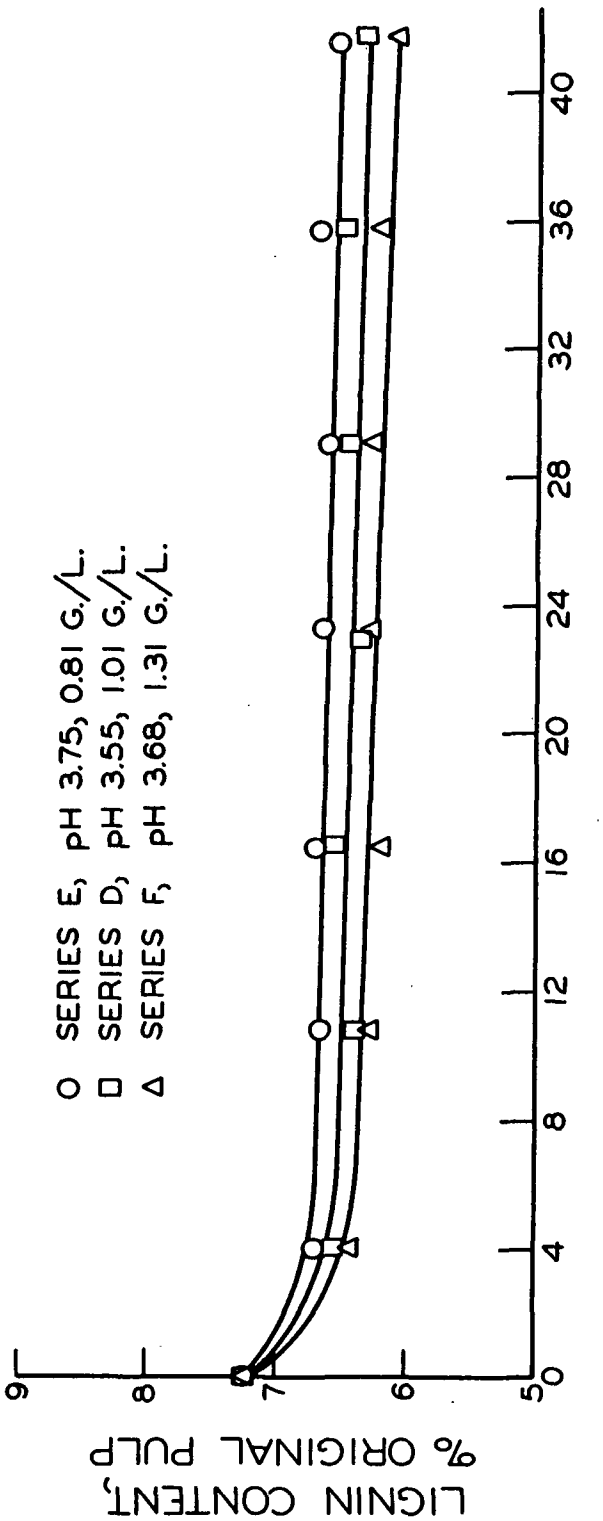


Figure 13. Delignification With Hypochlorous Acid

The chlorine solutions applied in this set of runs presumably possessed high potentials for lignin oxidation as high concentrations of hypochlorous acid were employed. Since delignification was minor, it appears that this reaction was ineffective under the chlorinating conditions. Residual chlorine values indicated that little or no consumption occurred in these experiments.

In the next set of chlorination runs, solutions containing both molecular chlorine and hypochlorous acid were employed. Preliminary work indicated drastic delignification occurred very rapidly when a reaction pH below 2.0 was used; therefore, these series were performed in the neighborhood of pH 3.0. Reactor calibration trials in this pH range indicated small variations would not seriously affect the course of delignification. Approximately 3% of the available chlorine is present as molecular chlorine at this pH with the remainder being hypochlorous acid. These runs are shown in Fig. 14.

As the chlorine concentration was increased, delignification became more extensive. Similar results have been reported in other chlorination studies. Using chlorine concentrations of 0.36 to 0.90 g./l., Chapnerkar (12) found delignification of a kraft pulp was promoted by increased applications of chlorine in a reaction period of three minutes to one hour. In another study of kraft pulp involving two levels of chlorine concentration, lignin removal was reported to be greater at the higher chlorine dosage (19). The same behavior has been observed with sulfite pulps as well (11,21).

Lignin removal at the lowest chlorine concentration was somewhat different in that its rate was relatively constant throughout the reaction period.

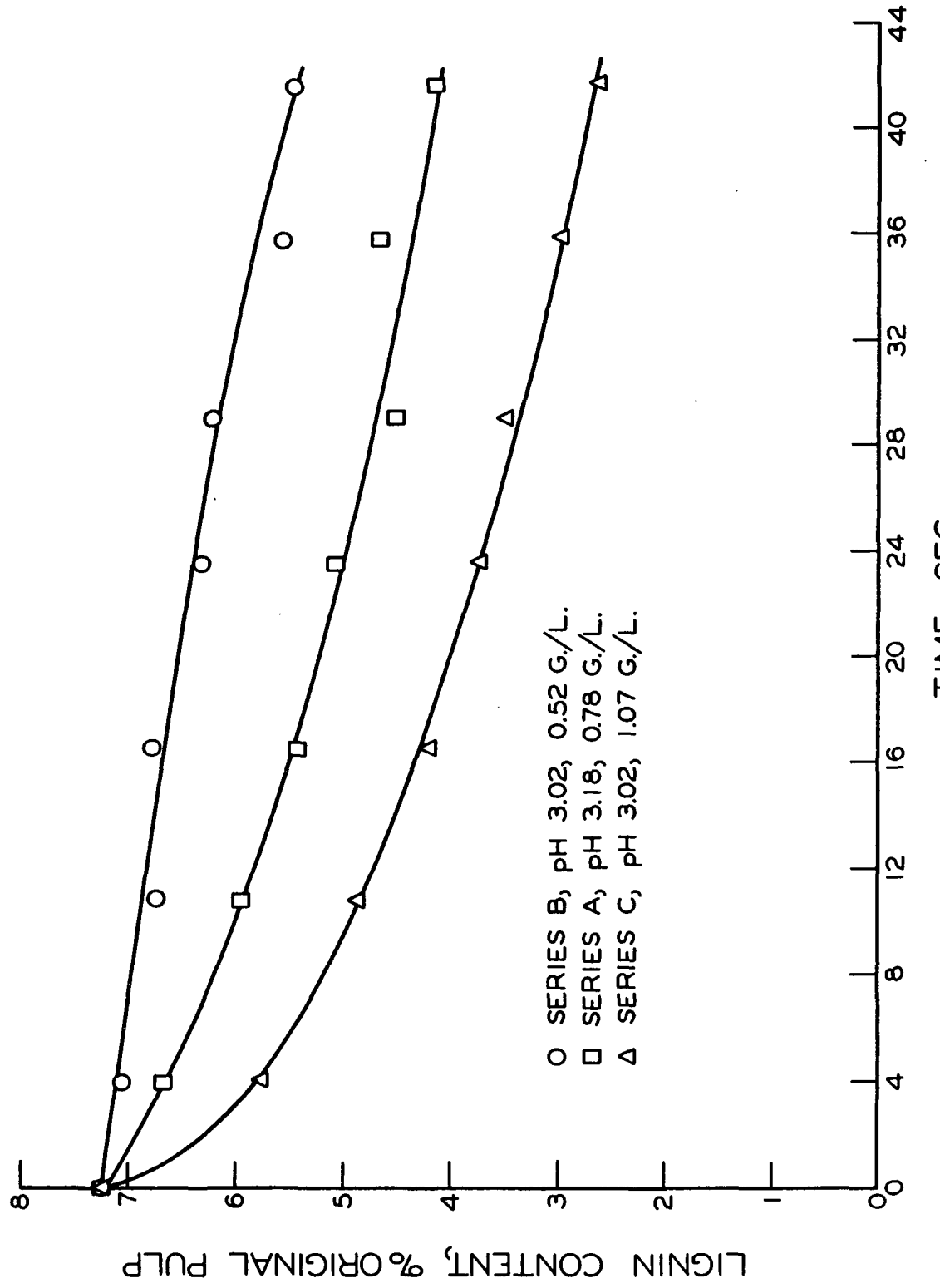


Figure 14. Delignification With Hypochlorous Acid and Molecular Chlorine

Since substantial lignin removal occurred in these series, an attempt was made to evaluate Equation (2). As an approximation, $f'(L)$ was assumed to be the Klason lignin content raised to some power:

$$-dL/dt = k'L^a \qquad (4)$$

where a = reaction order.

The smooth curves representing delignification in Series A and C fitted the data quite well, so they were differentiated graphically using a mirror. The slopes (dL/dt) determined at various L values were used to calculate a for the series. Reaction orders of 1.9 and 1.8 were obtained for Series A and C, respectively. This approach was not applied to the data obtained at the lowest concentration due to the apparent independence of $-dL/dt$ toward the lignin content.

Values for k' were calculated using the integrated form of Equation (4) with a being 1.8. Trends in the pseudo rate constants were observed for both Series A and C before relatively constant values were obtained. This behavior indicated the nature of lignin removal was changing in this early phase.

Equation (3) shows k' to be a function of chlorine concentration. This dependence was examined through use of the reciprocal of the time required to reach a specific level of delignification ($1/t_x$) as an approximation of k'. Such an approximation has been found to be useful in pulping studies (48,49). As seen in Fig. 15, the early stages of lignin removal were quite dependent upon the applied chlorine and this dependence changed as delignification progressed. A similar comparison was made using molecular chlorine concentrations rather than available chlorine values as shown in Fig. 16. Concentration variations between Series A and C appeared to be of greater significance in this case.

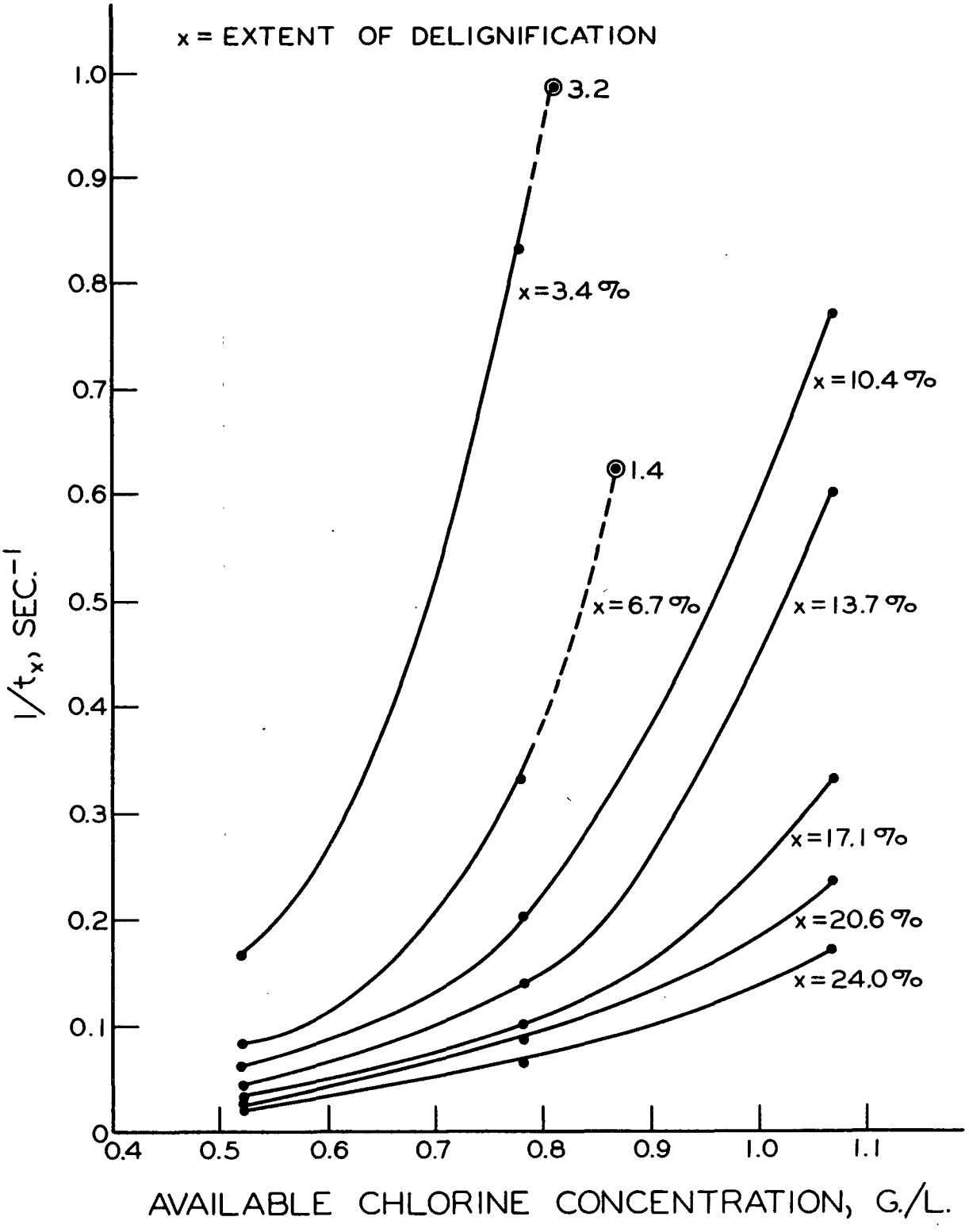


Figure 15. Dependence of $1/t_x$ on Available Chlorine

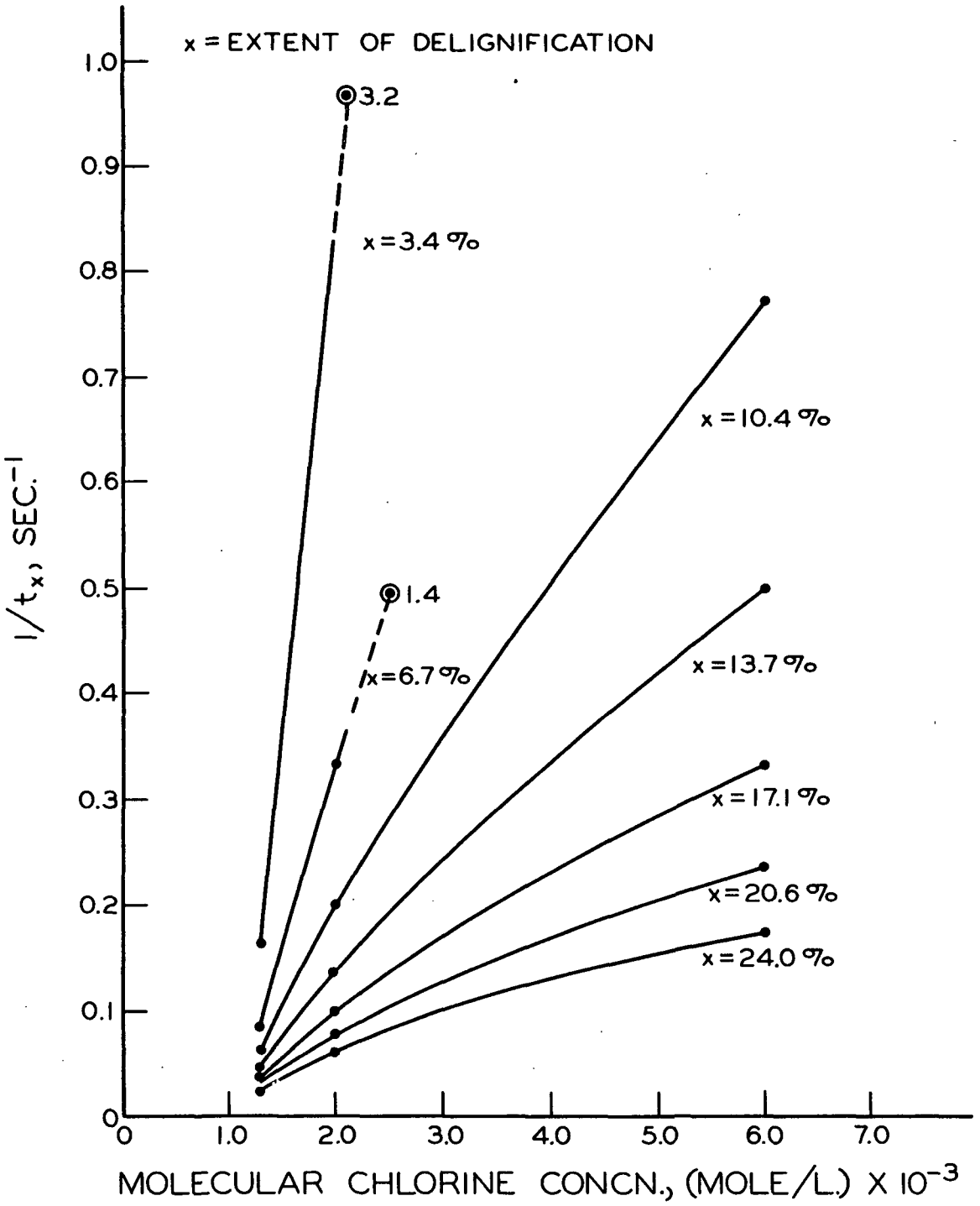


Figure 16. Dependence of $1/t_x$ on Molecular Chlorine

This behavior corresponded more closely to the response of lignin removal to chlorine concentration changes in the two series. It appeared then that the molecular chlorine concentration may be the more appropriate choice for C in Equation (3). The lack of lignin removal in the absence of molecular chlorine also supports this hypothesis.

Regardless of the concentration used, it is certain that k' was not a simple function of the applied chlorine. In view of the results of model compound studies, it is possible that the nature of the delignification reaction was changing in its early phase. A logical shift would be from a substitutive to an oxidative reaction as the controlling mechanism.

A second possibility involves the accessibility of lignin. As delignification progressed, lignin would become less accessible to the chlorine reagent. It has been stated that at longer reaction times lignin becomes less accessible to the reagent due to the accumulation of reaction products (11,12). Furthermore, extrapolation of chlorination behavior of pulp, wood, and model compounds has suggested that lignin accessibility is not a factor in the initial stages of the reaction (21,34).

The rates of bound chlorine in the three series are shown in Fig. 17. Chlorine contents increased fairly regularly throughout the reaction period. The chlorine contents in the unextracted pulps appeared to be proportional to the extent of delignification observed after extraction. This association was examined further by comparing the extents of organically-bound chlorine and delignification. For each reaction time, values were read from the smooth curves drawn through the delignification and chlorine content data for a series. These points are plotted in Fig. 18. There was a definite relationship between the bound chlorine and the extent of lignin removal.

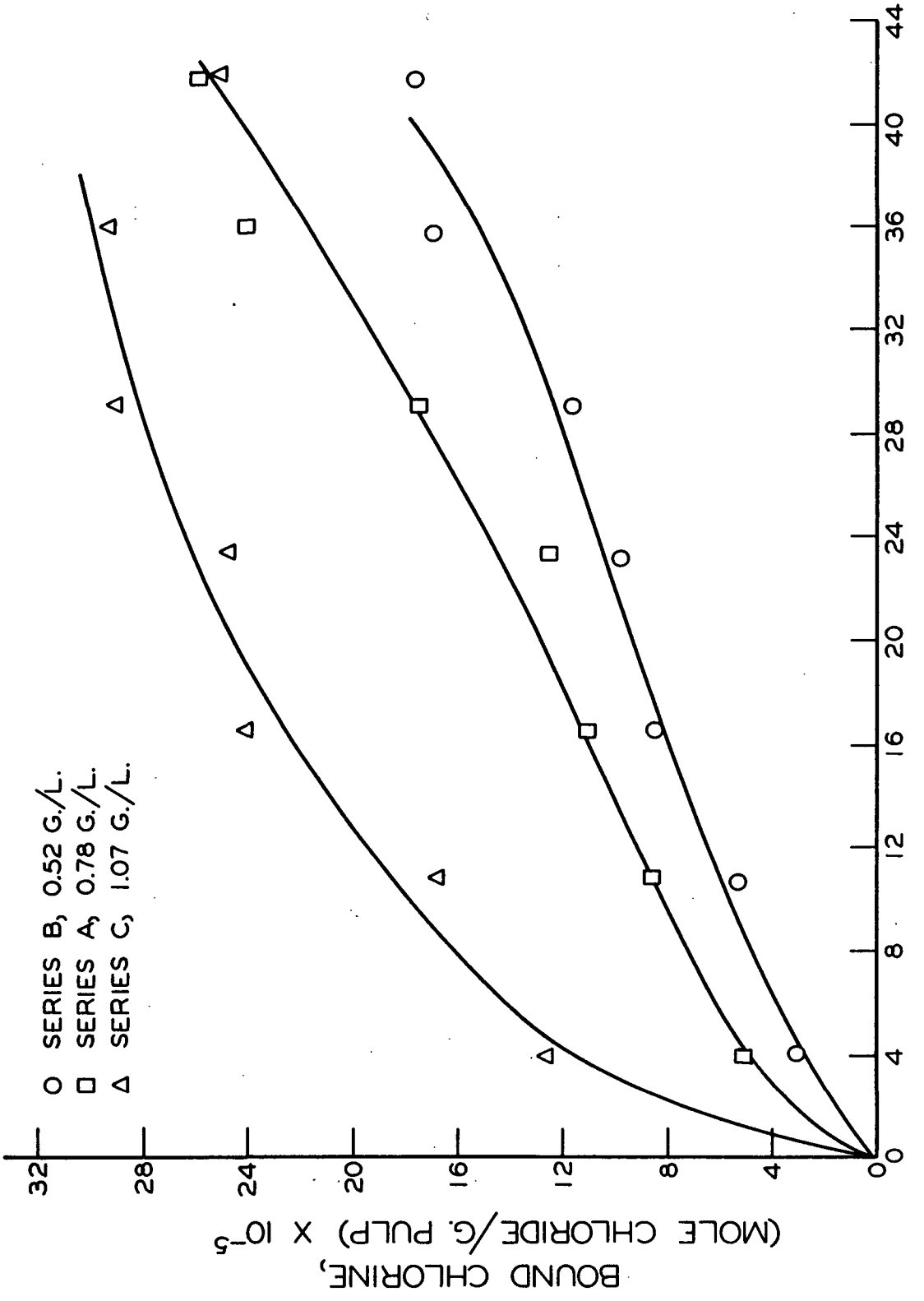


Figure 17. Effect of Concentration on Bound Chlorine

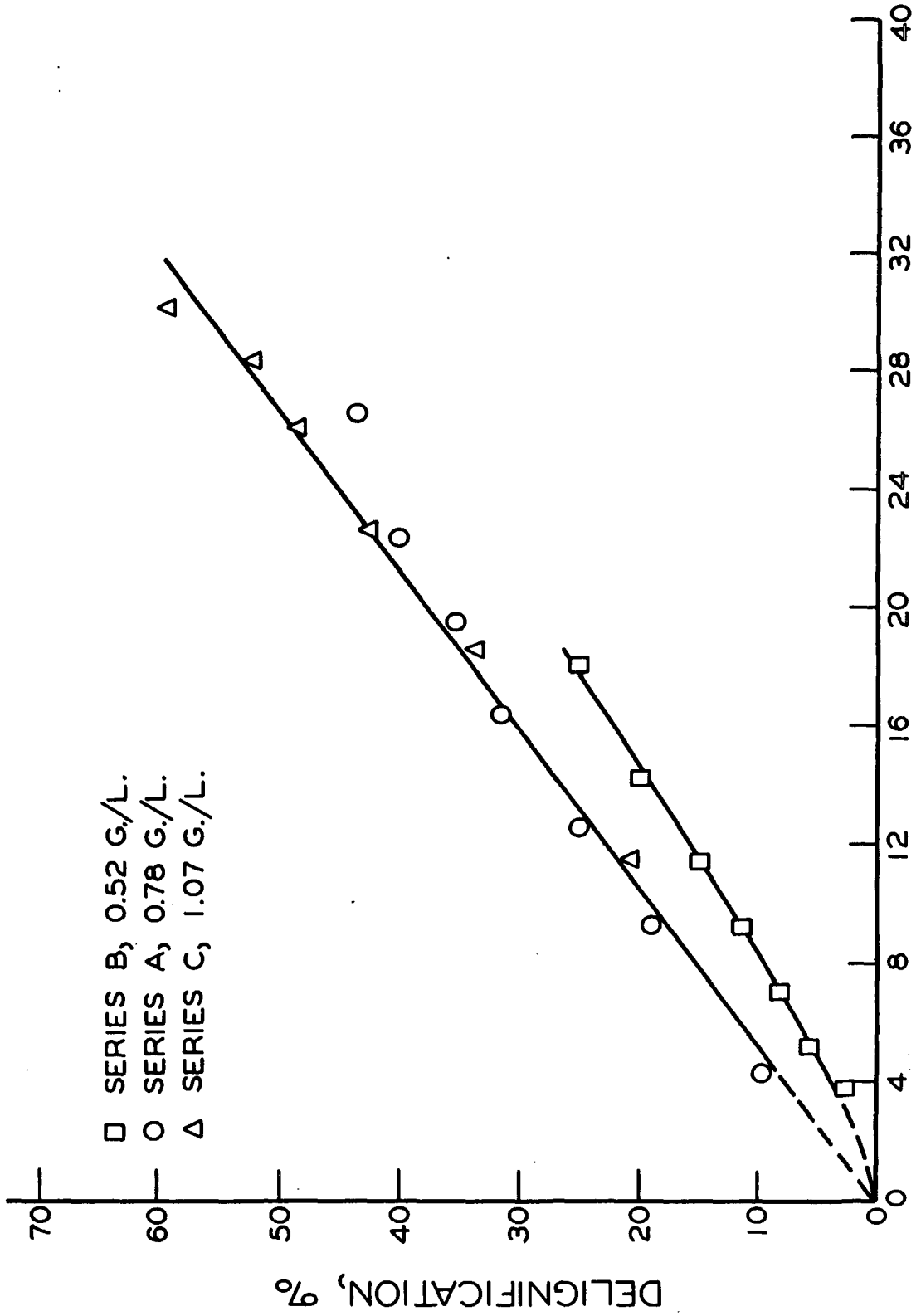


Figure 18. Effect of Concentration on Bound Chlorine-Delignification Relationship

In two previous studies of pulp chlorination, attempts have been made to establish similar relationships by measurement of organically-bound chlorine. White, et al. (27) reported difficulties in obtaining duplicate chlorine contents for a kraft pulp after chlorination unless exhaustive hot water washing was employed. This technique would remove a substantial portion of the chlorinated material. Hentola and Stone (50), in a study of a sulfite pulp, attempted to measure organic chloride from a difference in the total and inorganic chloride present after chlorination. Their results exhibited a high degree of scatter and did not represent a sound basis for definite conclusions regarding the relationship of delignification and bound chlorine in the pulp.

The relationship at the two higher chlorine concentrations can be represented adequately by a single line. However, the relationship was somewhat different at the lowest concentration, Series B. In this case, a particular extent of bound chlorine appeared to correspond to lower lignin removal. Apparently, the nature of the delignification reactions changed as chlorine concentration was increased from 0.52 to 0.78 g./l. Further increase in concentration to 1.07 g./l. caused no significant change in the bound chlorine-delignification relationship. Possibly, at the lowest concentration, chlorine diffusion into the lignin structure was relatively small in comparison with the rate of substitutive reactions. In this case a larger quantity of chlorine would have been involved in secondary reactions which would not contribute to lignin solubilization. As a result, a particular level of bound chlorine would correspond to a lower extent of lignin removal as observed in Series B.

The apparent independence of delignification rate from lignin content found in this series would result from the emphasis on the diffusing reagent rather than the chemical reaction. This line of reasoning is in accord with the experimental data.

The total chlorine consumption values in these runs averaged less than 6%; therefore, the use of a pseudo rate constant was permissible. Bound chlorine values were compared with total consumption values in Series A and C. The average differences between these two values at the seven reaction times were 2.6 and 2.9% for Series A and C, respectively, with bound chlorine being lower in nearly every instance. Although the possible errors inherent in this comparison would tend to reduce these differences, it is evident that oxidation occurred in the runs.

This consumption could have accounted for up to 50% of the total chlorine consumption. In Series A and C, 0.54 gram of chlorine was bound to the pulp for each gram of lignin removed. It is estimated that the maximum ratio of about 1.0 gram of chlorine per gram of lignin would apply in these two series. This value is somewhat below the ratio of 1.3 reported by Chapnerkar (12) and Carmody and Mears (20). One would expect less secondary reaction in the present system; therefore, it is reasonable that a lower value was obtained.

The poorer agreement between bound chlorine and total consumption observed in Series B is attributed to reduced accuracy of the latter measurement at the low concentration involved in this set of experiments.

Samples of Series A and C pulps were analyzed for viscosity to estimate the influence of concentration changes on the cellulose portions of the fibers. There was little difference between the average viscosities for the two runs, being 17.7 cp. and 16.5 cp. for Series A and C, respectively. The higher concentration yielded the greater viscosity reduction from the original value of 21.0 cp.

CHLORINATION TEMPERATURE

In view of previous results, little or no temperature dependency of delignification was expected in the absence of molecular chlorine. The set of runs performed at 8.8°C. and pH 4.03 indicated lignin removal was the same as that observed at higher temperatures in this pH region.

When molecular chlorine is present, the effect of temperature is more pronounced. Delignification was found to increase as the reaction temperature increased in a number of other studies involving reaction times of several minutes to several hours. Giertz (11) and Eriksson and Stockman (19) observed a maximum in the improvement of lignin removal with increasing temperature. The former study involved chlorination of an "artificial silk" pulp and the latter study concerned treatment of a sulfate pulp.

In the present system, it was found that the effect of temperature variations was affected by changes in the molecular chlorine concentration. With reference to Fig. 19, it is seen that a temperature reduction from 22.7 to 16.1°C. yielded a slight decrease in lignin removal. The molecular chlorine concentrations in these two series were calculated to be 0.0028 and 0.0025 mole/l. at 22.7 and 16.1°C., respectively. A further temperature decrease to 8.7°C. yielded a regain in the extent of lignin removal. This anomalous behavior resulted from an increase in the molecular chlorine concentration to 0.0048 mole/l. in this series. The increased concentration resulted from a slightly lower reaction pH and a reduced hydrolysis of chlorine.

A second examination of temperature dependency was made at a higher chlorine concentration. Due to a shortage of pulp, only two series were included in this comparison. A definite reduction in the extent of lignin removal

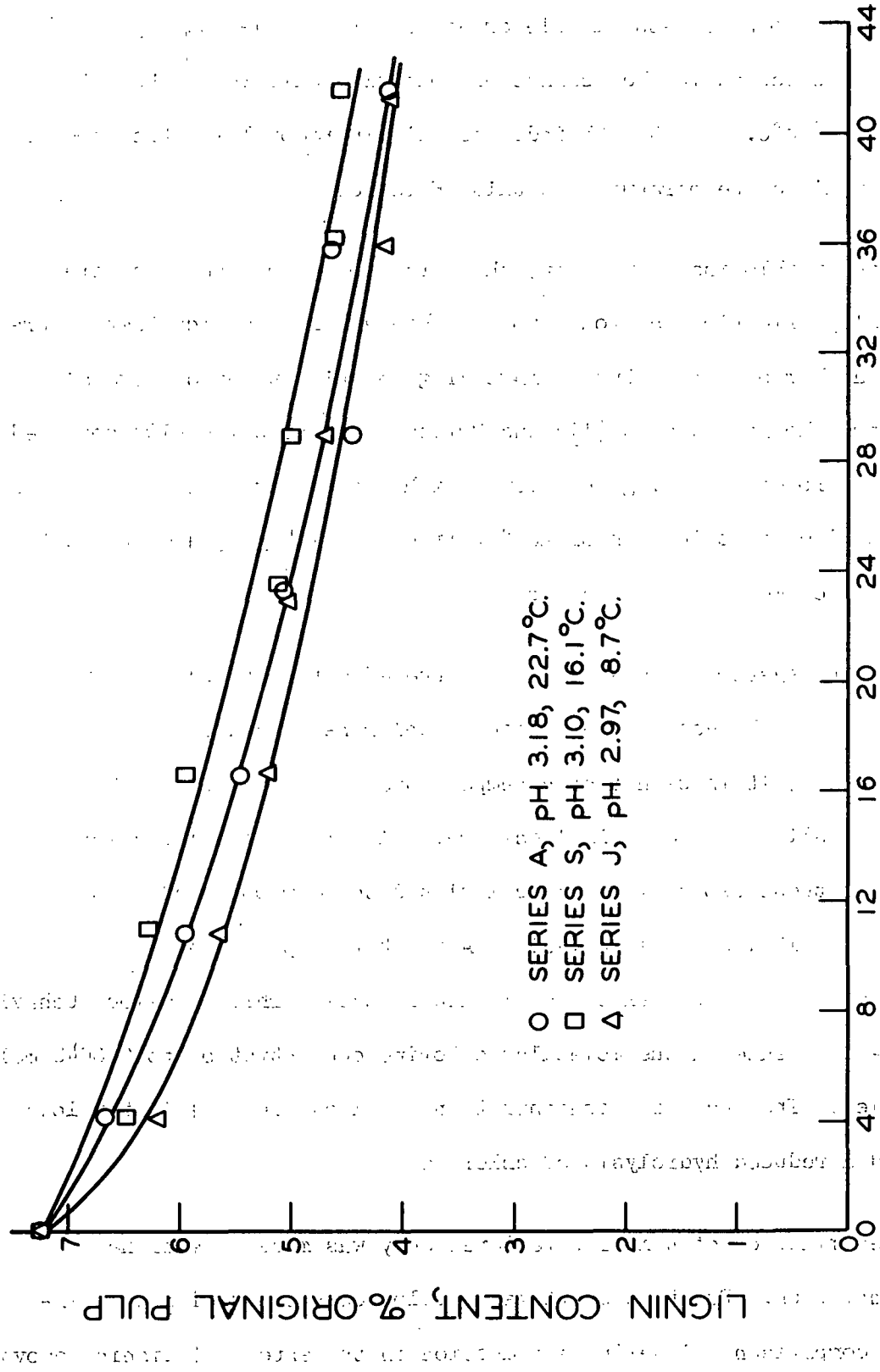


Figure 19. Effect of Temperature on Delignification at 0.78 g./l. Available Chlorine

was observed as the reaction temperature was decreased from 22.7 to 14.0°C. as seen in Fig. 20.

Over the reaction period, Series S values were from 2.6 to 11.1% higher than corresponding A lignin contents. A similar comparison between Series V and C showed the former series' lignin contents were 14.1 to 32.3% higher than corresponding C values. The 8.7°C. temperature difference in Series C and V yielded a lignin content difference of about 1.0%; in Series A and S, the lignin content difference was approximately 0.5% for a 6.6°C. temperature variation. The relatively small change in temperature differences employed in the two sets of series was not sufficient to account for this large change. It would appear that delignification became more sensitive to temperature in the higher chlorine concentration series. Eriksson and Stockman (19) also noted that the effect of temperature on lignin removal was influenced by the chlorine dosage when chlorination proceeded for one hour.

The levels of organically bound chlorine for the 3 low-temperature series S, J, and V increased over the reaction duration as seen in Fig. 21. The relationships for chlorine content and delignification for the lower concentration Series A and S are shown in Fig. 22. Lower chlorine contents were obtained in Series S when compared to Series A. Furthermore a particular level of bound chlorine in the former series corresponded to a reduced extent of lignin removal compared to that observed in the latter set of runs.

At the higher concentration used in Series V and C, there was a reduction in the extent of bound chlorine in the former series. In addition, a particular level of bound chlorine corresponded to a lower lignin removal at 14°C.; the extent of this difference is shown in Fig. 23. In Series S and V the total consumption of chlorine was close to that bound to the pulp. In Series A and C

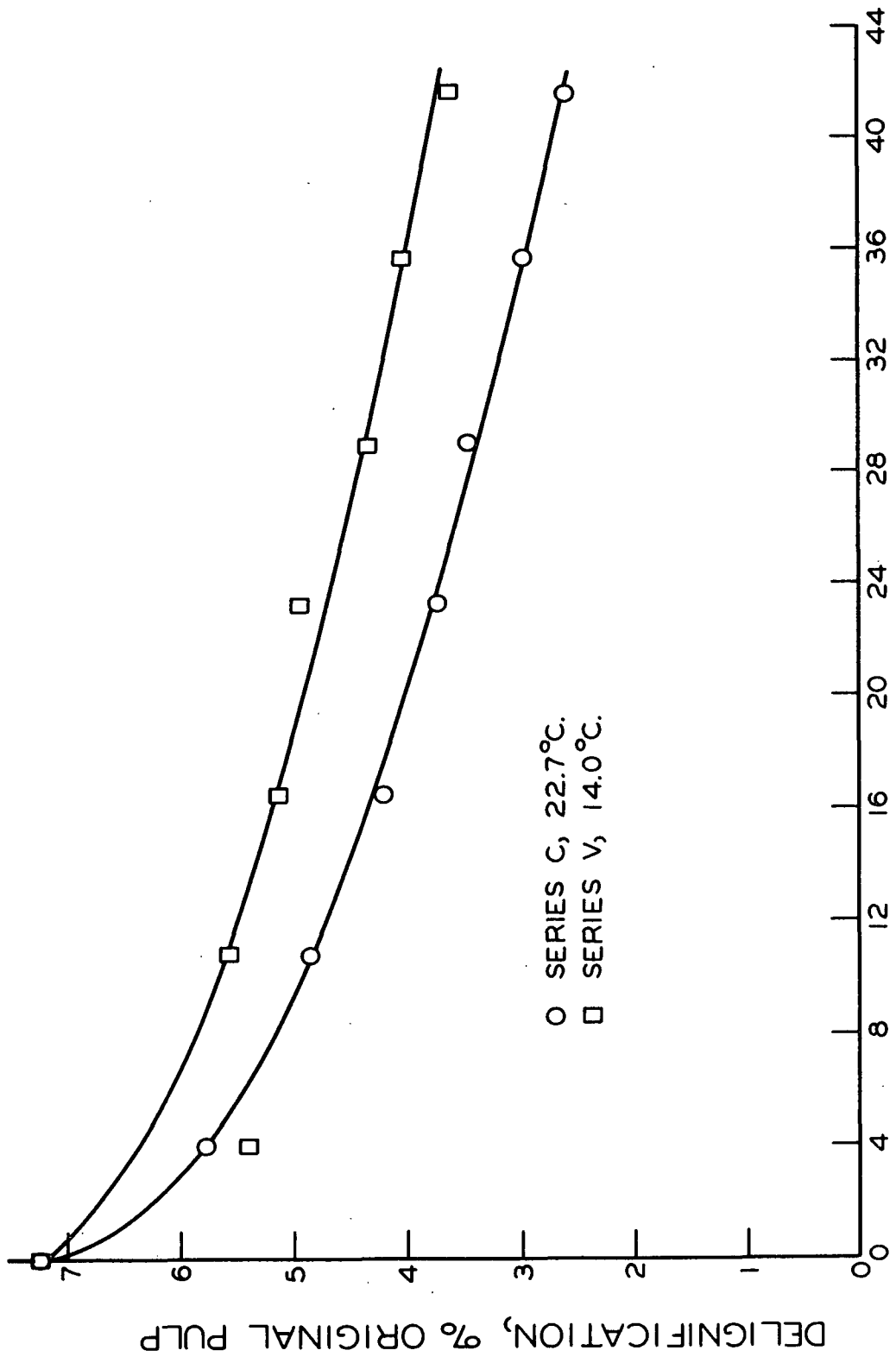


Figure 20. Effect of Temperature on Delignification at 1.07 g./l.

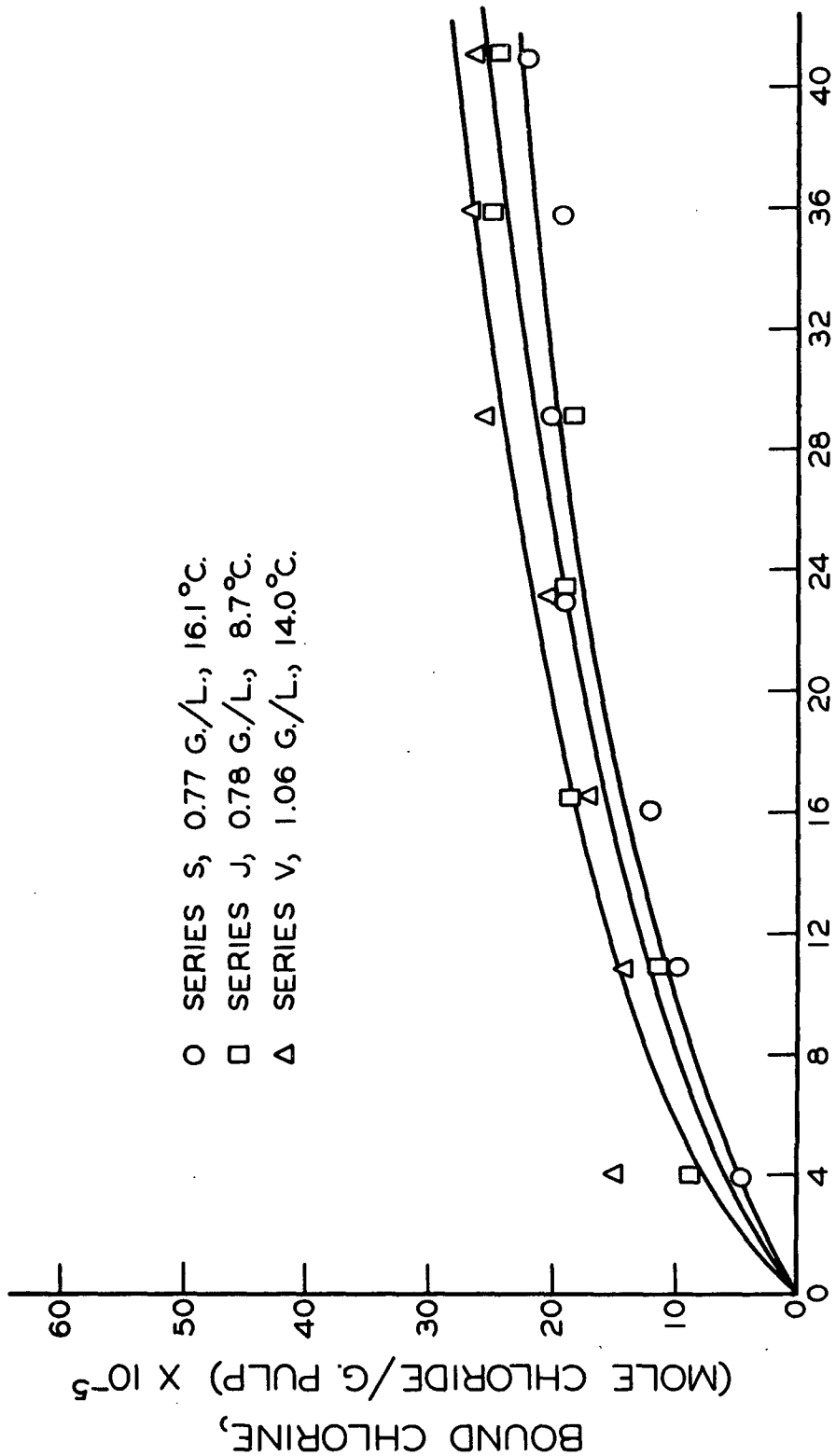


Figure 21. Bound Chlorine *vs.* Reaction Time at Low Temperatures

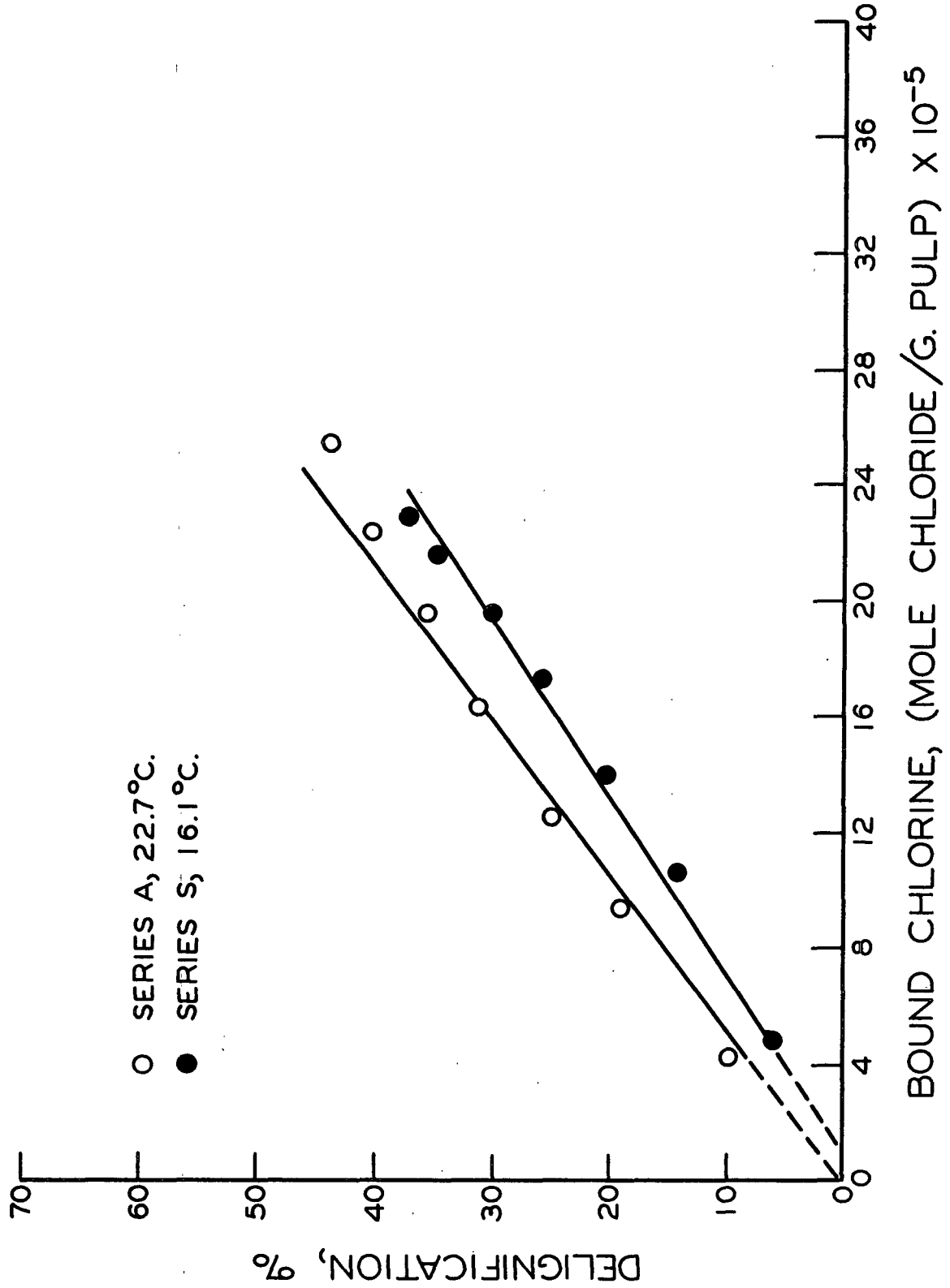


Figure 22. Bound Chlorine vs. Delignification at 0.78 g./l.

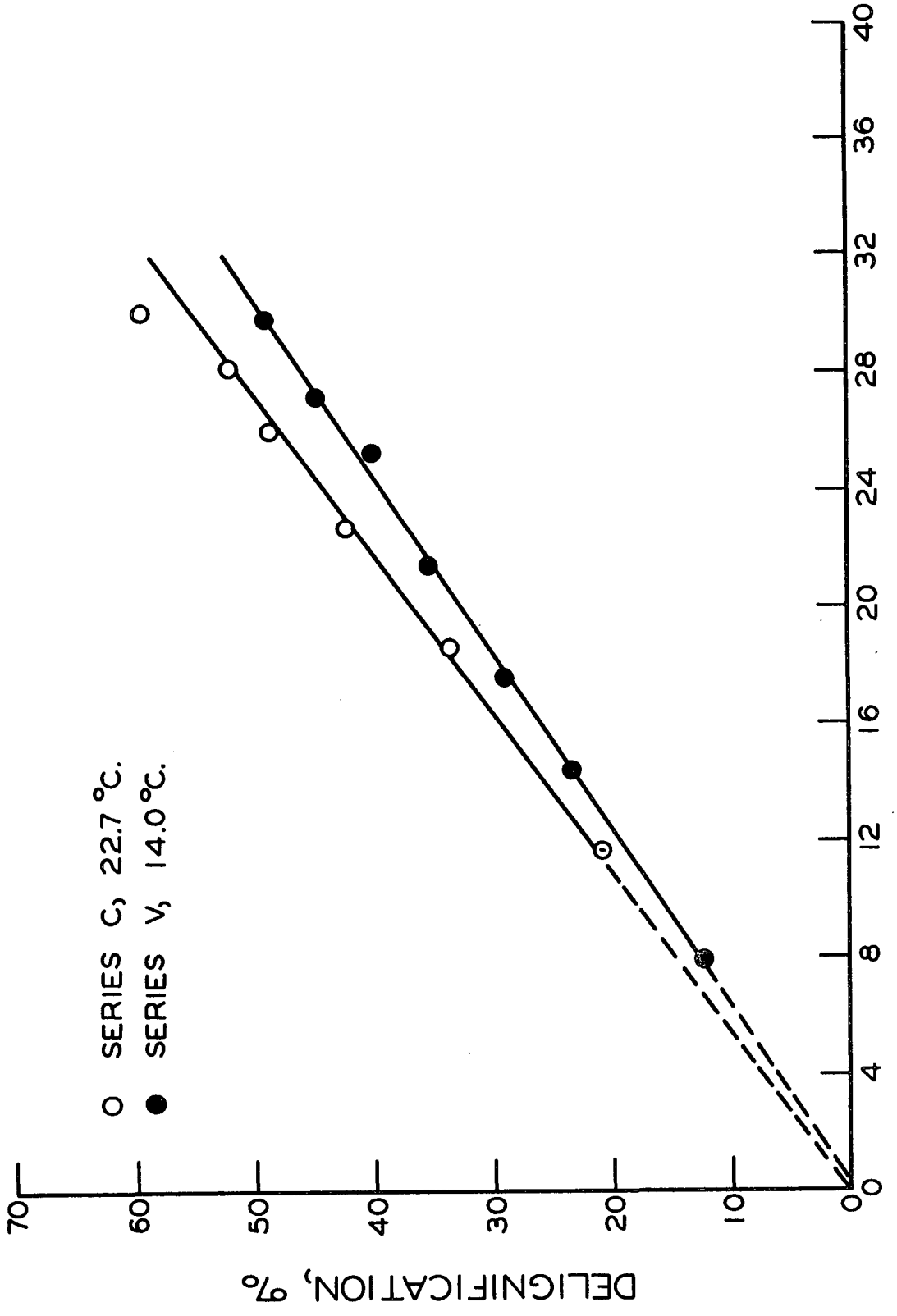


Figure 23. Bound Chlorine vs. Delignification at 1.07 g./l.

a much greater proportion of the total consumption could not be attributed to substitutive reactions. On the other hand, the levels of bound chlorine were not substantially affected by the temperature variations. This behavior indicates that oxidation was influenced to a greater degree by temperature variations. Other studies have indicated this relative sensitivity of the two reactions is the same in later stages of chlorination of both sulfite and sulfate pulps (11,12,19,21). It is believed that the increased temperature sensitivity observed in lignin removal in Series C and V resulted from a greater contribution of oxidation to delignification in these series. This would be expected if the extent of oxidative consumption of chlorine was related to the level of bound chlorine.

The relative sensitivities of the substitution and displacement reactions to temperature changes are not known. As a result, the possible importance of shifts in the proportion of bound chlorine attributable to each of the two mechanisms cannot be evaluated.

Since Series V data could be represented by a well-defined smooth curve, graphical integration was employed to estimate a in Equation (4). A value of 2.0 was obtained which agreed fairly well with the reaction orders of 1.9 and 1.8 determined for Series A and C, respectively. These few determinations indicated a was independent of chlorine concentration and reaction temperature. It was believed that the construction of smooth curves for Series S and J would be arbitrary due to greater scatter in the data; therefore, reaction orders were not calculated for these sets of data. However, k' values were calculated for these series using a reaction order of 1.8. A relatively small trend was observed in Series S values indicating the applicability of the reaction order. A somewhat larger trend was noted in Series J. Pseudo rate constants for Series C and V also displayed an initial variation of k'. A part of this change is attributed to the loss of easily removed material similar to that observed in the higher pH region.

A shift in the nature of the delignification reactions could have contributed to this initial variation also.

The trends in the pseudo rate constants are shown in Table X. It is seen that $\underline{k}'$ nearly doubled with the 8.7°C. temperature increase employed in Series C and V. Eriksson and Stockman (19) reported that an 8°C. temperature rise in the chlorination of a kraft pulp caused a doubling of the reaction rate.

TABLE X

TRENDS IN PSEUDO RATE CONSTANT[a]

$\underline{k} \times 10^{-3}$

Series	A	S	J	C	V
Chlorine concn., g./l.	0.78	0.77	0.78	1.07	1.06
pH	3.18	3.10	2.97	3.02	3.05
Temperature, °C.	22.7	16.1	8.7	22.7	14.0
	4.8	6.5	7.0	13.0	17.0
	4.2	3.0	5.4	9.0	5.7
	4.1	2.8	4.9	8.6	5.0
	3.6	3.7	3.7	7.8	3.9
	4.1	3.1	3.6	7.0	4.7
	3.0	3.2	4.1	7.6	4.3
	3.5	2.7	3.5	7.9	4.2

[a]Based on a reaction order of 1.8.

Viscosity measurements indicated that temperature reductions lessened cellulose degradation as expected. The difference in viscosities of Series C and V samples was relatively small. A much greater difference was observed in Series A and J, probably as a result of the greater temperature difference and a reduced chlorine concentration. The increased viscosities of Series J over that measured for the original pulp indicated that a loss of low molecular weight material occurred.

REACTION pH

Generally, the importance of pH has been attributed to its effect on the molecular chlorine concentration present in the chlorinating medium since it is known that, at ordinary temperatures, the diatomic chlorine molecule is the reactive species in substitution. In addition, the action of electrophilic catalysts is required in this reaction; therefore, the increased quantity of hydrogen ions should facilitate substitution (51).

In the present study, lignin removal was observed to increase considerably as the reaction pH was lowered. This behavior is shown in Fig. 24. The sensitivity of delignification to the presence of molecular chlorine and acidity is illustrated quite well by comparing the series designated B and F. The former set of runs was performed with about five times the molecular chlorine and about 1/3 of the available chlorine employed in the latter series. The hydrogen ion concentration in Series B was about twice that used in Series F. Delignification was found to be somewhat greater in Series B. This behavior was further indication that the molecular chlorine had a more direct relationship to lignin removal than did the available chlorine concentration.

In a previous study of kraft pulp chlorination, an "instantaneous" removal of 55% of the original lignin was observed after chlorine treatment and alkaline extraction (12). This extensive initial delignification shows that the drastic lignin removal which occurred in Series P is not characteristic of only the present reaction system. The large initial lignin removal and high levels of bound chlorine indicated that diffusion was unimportant at this low reaction pH.

The extent of bound chlorine, plotted as a function of reaction time in Fig. 25, reached a maximum in Series P and then declined slightly. Grangaard (21)

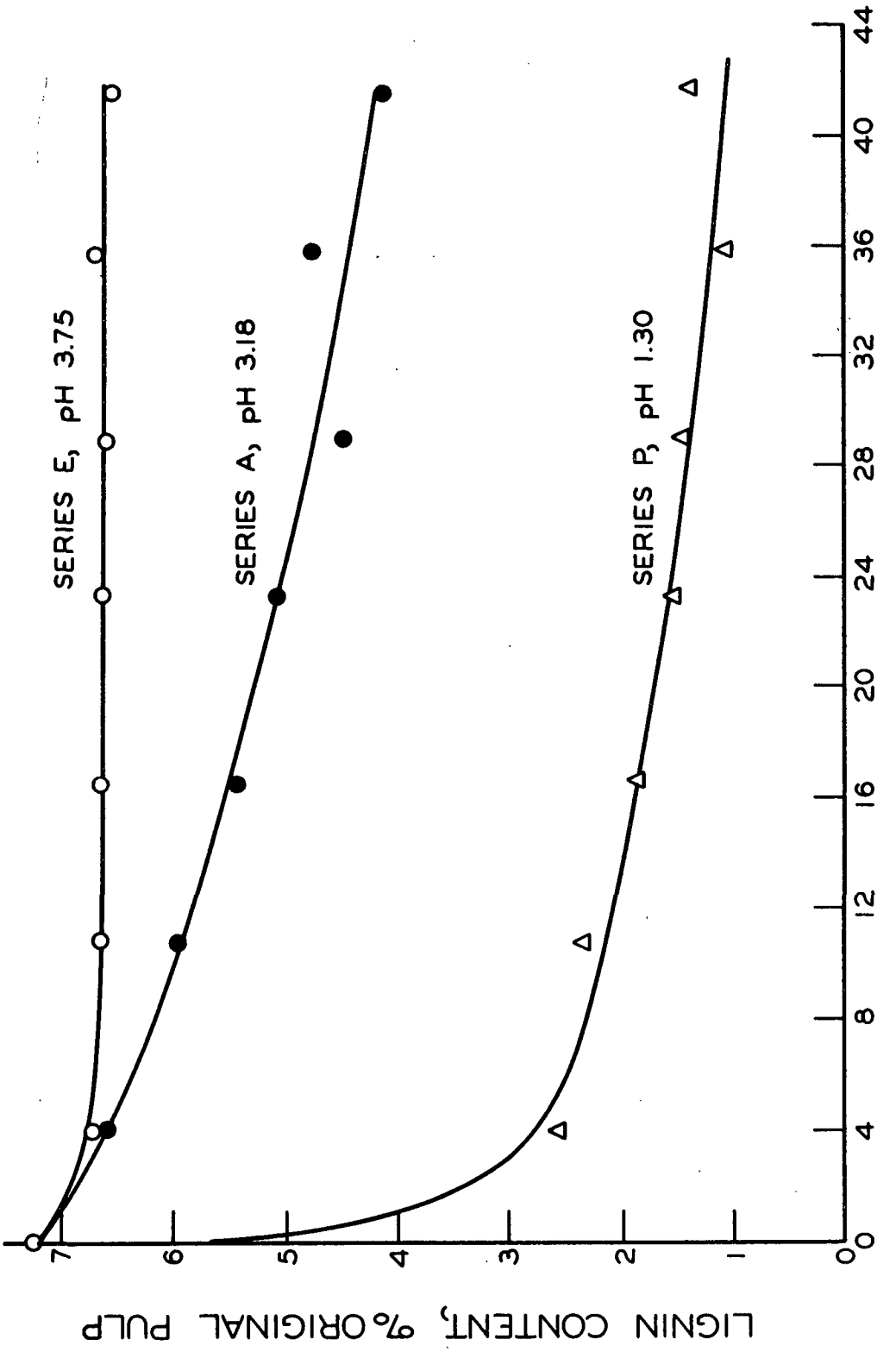


Figure 24. Effect of pH on Delignification

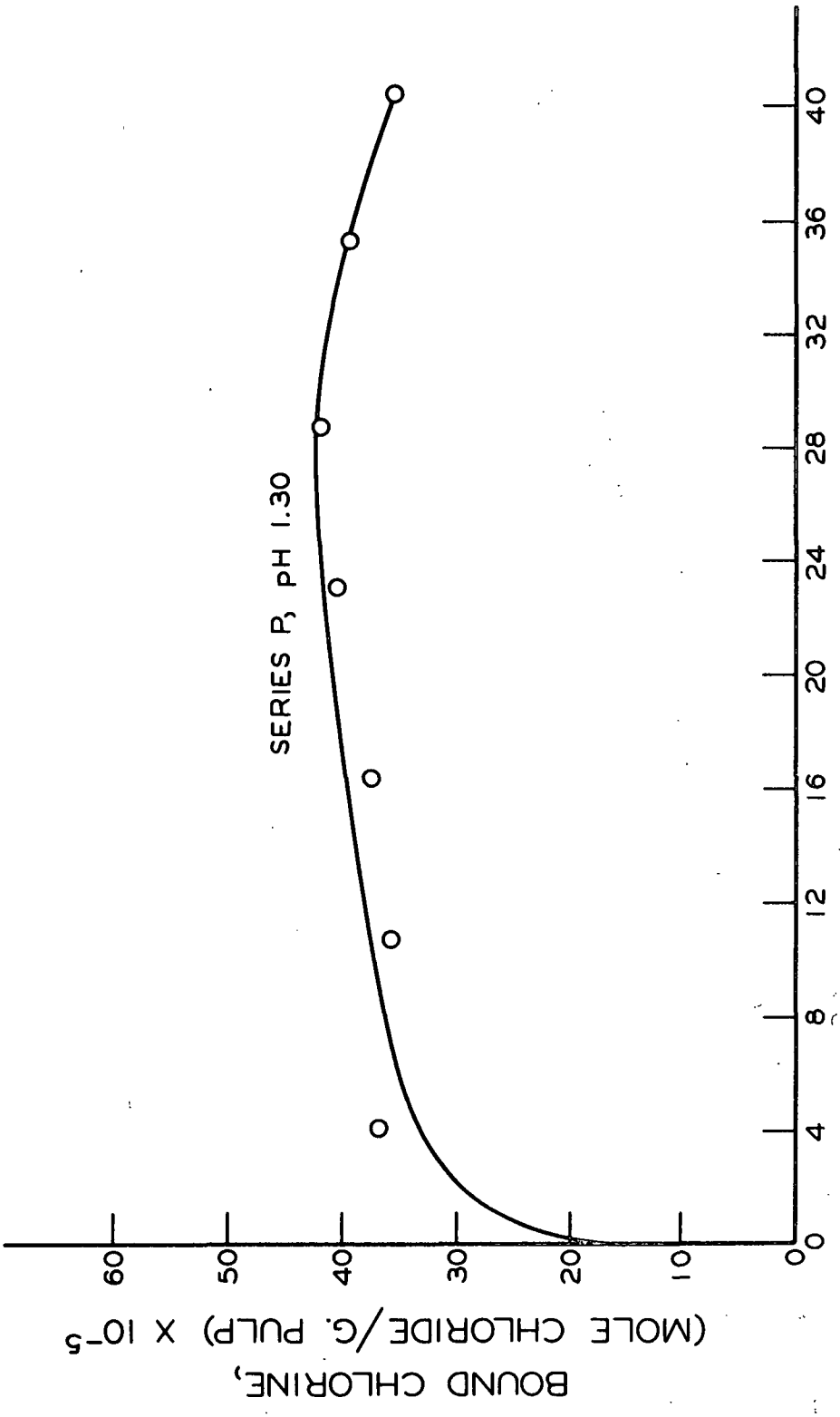


Figure 25. Bound Chlorine vs. Reaction Time at pH 1.3

reported similar behavior for chlorination of a sulfite pulp. Hentola and Stone (50) and Jansen and Bain (23) reported that substitution was enhanced by a lower reaction pH. The same association was found in the present system.

In the series of runs performed at pH 1.3, 11% of the applied chlorine was consumed while the maximum consumption attributable to substitution reached approximately 5%. This series, in conjunction with Series A and C, indicated that oxidation increased parallel with the extent of bound chlorine. In this respect, Grangaard has suggested substitution sensitizes lignin to oxidative attack (21). Due to the complexity of the lignin structure, the influence of substitution on its reactivity toward oxidative agents is difficult to envision. One possible mode of sensitization would be through increased oxidation of the displaced side chain. On the other hand, a side reaction, such as demethylation, which parallels substitution may enhance oxidation.

The bound chlorine-lignin removal relationship for Series P appeared to be an extension of that observed in Series A and C as seen in Fig. 26. Evidently the greater extents of both bound chlorine and oxidative consumption of chlorine in Series P represented only an increase rather than a change in the role of oxidation in delignification.

An extensive loss of viscosity was observed when the pulp was treated with the highly acidic chlorine solution in Series P. A sample of the original pulp having a viscosity of 21 cp. was treated with hydrochloric acid under conditions simulating those employed in Series P; a loss of viscosity down to 12.9 cp. occurred. This loss accounted for a significant portion of the viscosity reduction to about 8.5 cp. measured for the Series P samples. It is believed that the grinding treatment contributed to the loss of viscosity through fiber damage.

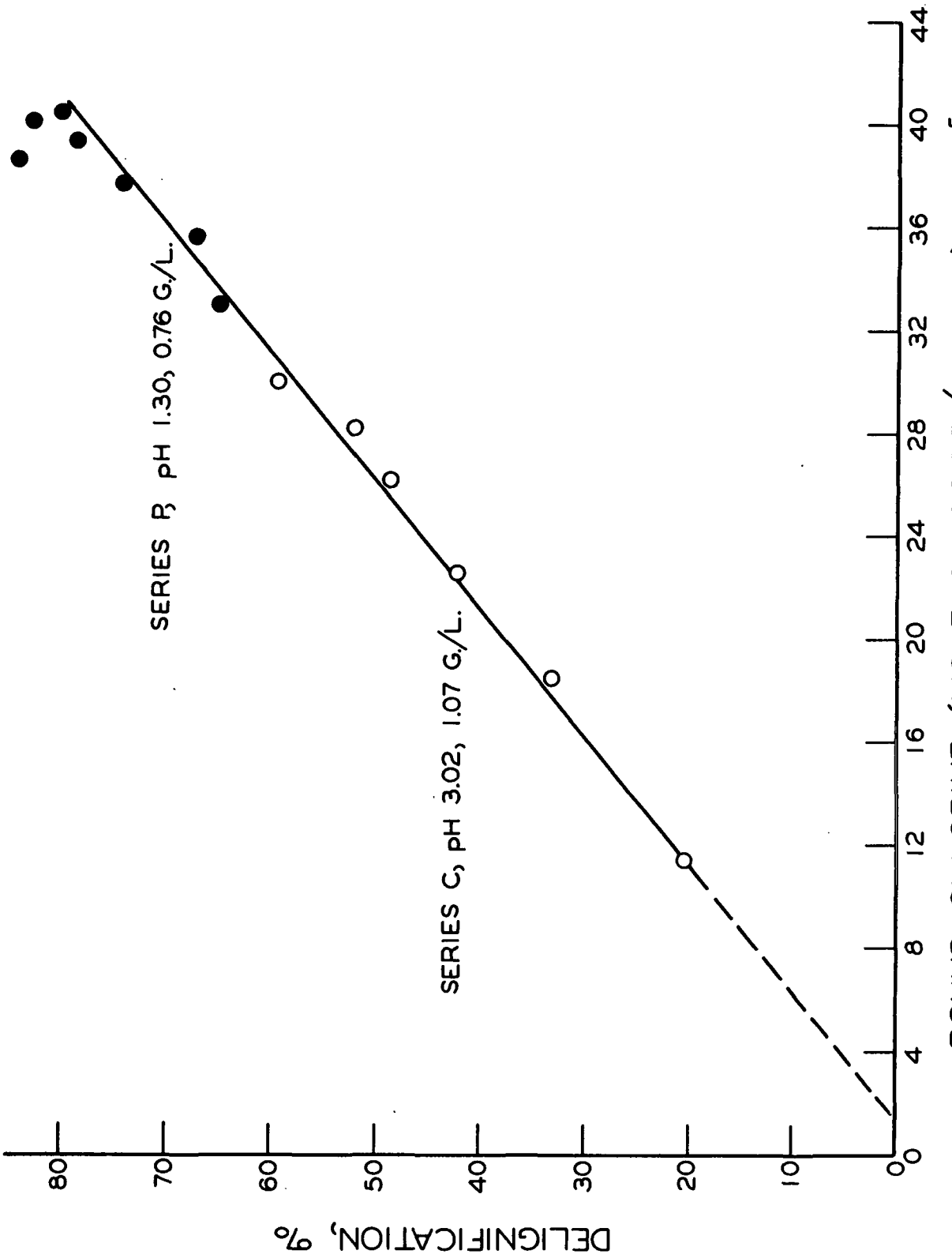


Figure 26. Comparison of Bound Chlorine vs. Delignification at Two pH and Concentration Values

COMPARISON OF TWO KRAFT PULP MEALS

The data presented so far were obtained from chlorinations of a single pulp meal (PU1). It was desired to confirm these results so a second pulp meal was chlorinated. It is known that dissimilar pulps respond differently to chlorination (12,18); therefore, a second kraft pulp (PU2) having a higher lignin content was employed. Two reaction conditions used in the chlorination of PU1 were duplicated for the treatment of PU2. The comparisons of PU1 and PU2 runs are shown in Fig. 27.

The extent of lignin removal from PU2 was minor when the presence of molecular chlorine was minimized. The delignification observed in Series L for PU2 was quite similar to that found in Series F for PU1.

At a reaction pH of slightly greater than 3.0, PU1 and PU2 exhibited similar delignification curves also. The PU1 curve for Series C was shifted on the time axis to examine the coincidence of the two lignin removal curves. This was accomplished by adding 16.7 seconds to each of the reaction times of Series C. As seen in Fig. 28, a single curve can be used to represent both sets of data. Only the original lignin content of Series C did not fall close to the combined delignification curve. The runs performed in the pH region from 3.6 to 4.0 exhibited an initial loss of lignin. If a similar loss is assumed to occur in Series C, the "effective" initial lignin content will fall much closer to the combined delignification curve.

This behavior indicated the over-all course of lignin removal was the same for both pulps and a single rate expression can be used to describe delignification of the two pulps. However, graphical integration of the Series N curve yielded a reaction order of 1.6 which was somewhat below that obtained in previous series. Along the same line, it is of interest to compare the relationships of bound

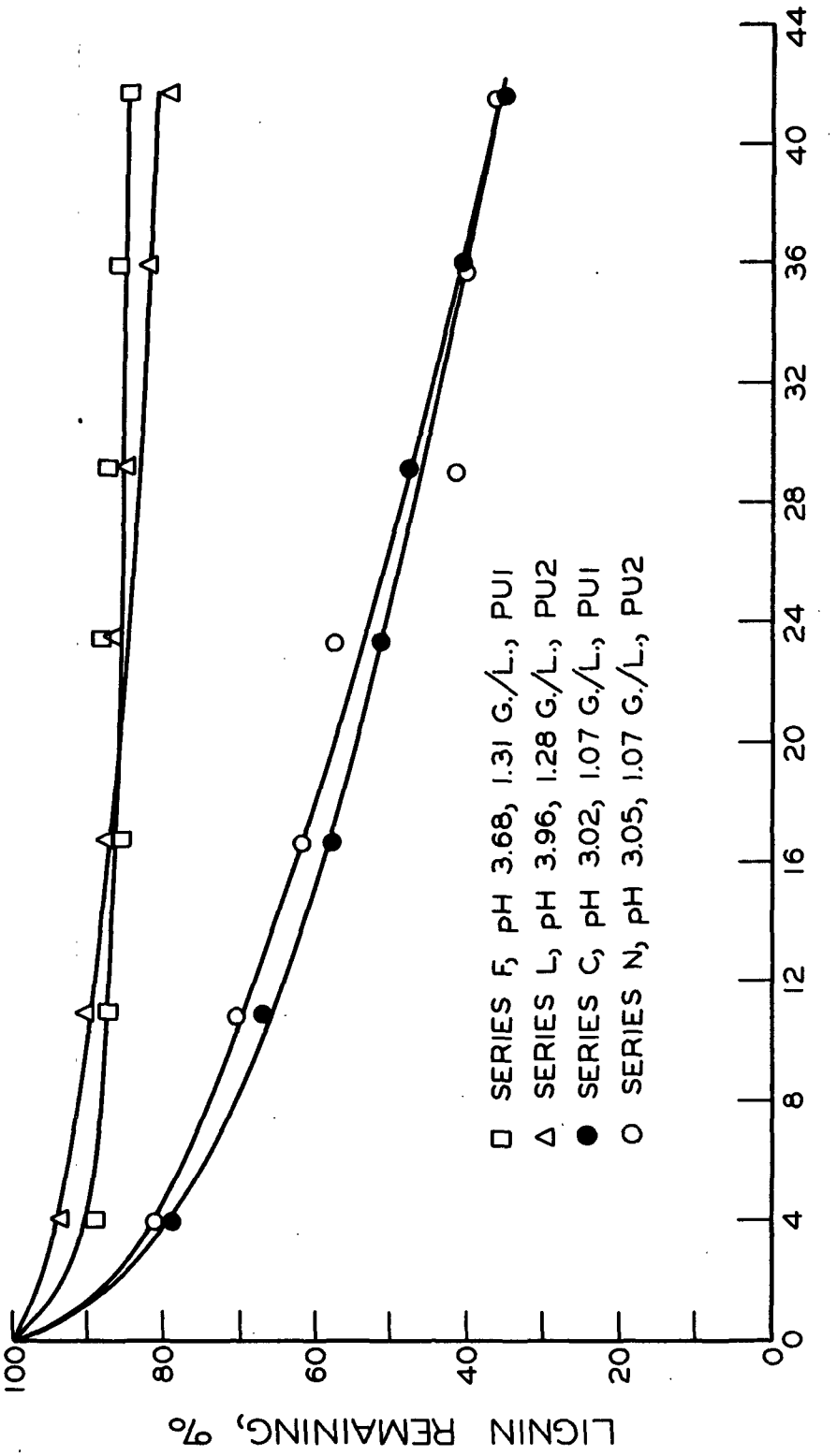


Figure 27. Comparison of Delignification of Two Kraft Pulp Meals

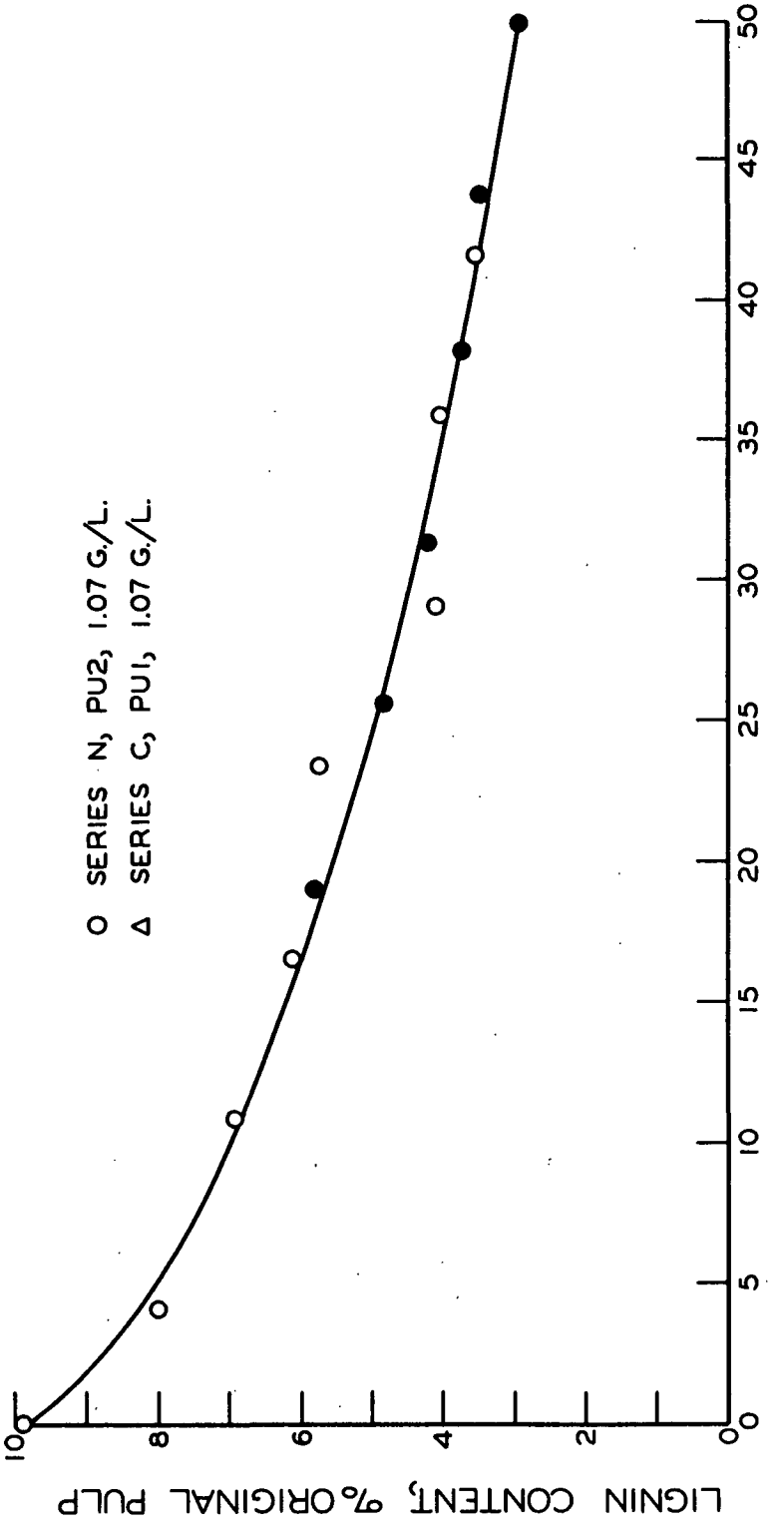


Figure 28. Composite Delignification Curve for Kraft Pulp Meals

chlorine to lignin removal for Series C and N. This comparison is presented in Fig. 29. In this case the chlorine contents are based on lignin rather than pulp. It was found that less bound chlorine was required to reach a particular level of delignification in Series N.

Since PU1 was pulped to a somewhat lower lignin content, one would expect the lignin in this pulp to be less accessible. As a result greater penetration into the fiber would be required to remove a specific percentage of lignin from PU1 than from PU2. If this is the case, the opportunity for secondary reactions involving previously reacted lignin would be greater with PU1. This line of reasoning could account for the differences in behavior of the two pulps.

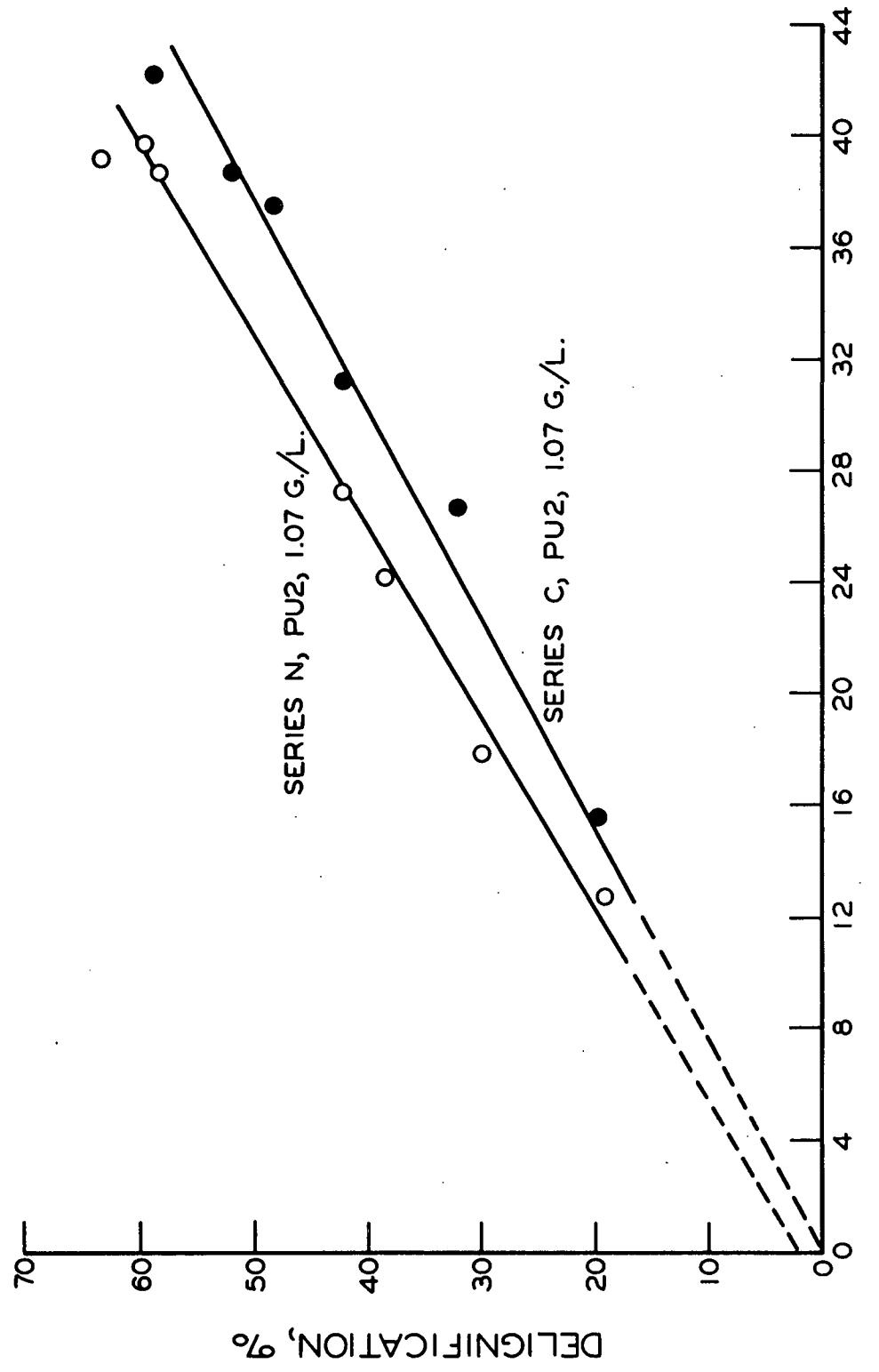


Figure 29. Bound Chlorine-Delignification Comparison of PU1 and PU2

CONCLUSIONS

Throughout the preceding discussion of the experimental results, various indications regarding the rate, extent, and nature of delignification were noted. These factors are considered here in relation to one another so that a coherent picture of the lignin removal may be presented. Unless otherwise noted, this discussion involves results obtained from chlorination of PU1.

The evidence indicated that the molecular chlorine concentration was a primary factor in the initial phase of delignification. Any change in the reaction conditions which increased this concentration was found to promote the extent of chlorine organically bound in the pulp. A definite relationship between increasing levels of bound chlorine and improvement in the extent of delignification was found to exist for all reaction conditions. It was found that large changes in acidity and molecular chlorine concentration caused no significant alteration in the relationship of bound chlorine with lignin removal. This observation was an important contribution in establishing the degree to which kraft pulp delignification is dependent on substitutive reactions. Previous attempts to clarify this relationship have dealt primarily with sulfite pulps; and, in those cases where kraft pulps were considered, only reaction durations of several minutes to several hours were considered.

It is believed that the chain displacement mechanism observed in lignin model compound studies (28-30) is the important substitution reaction. However, since a single relationship between bound chlorine and lignin removal was not obtained, other factors were involved in the over-all delignification reaction.

Previous studies of sulfate pulp chlorination involving various reaction conditions have indicated that oxidation contributes to delignification. It was

found in the present study that oxidative consumption occurred in the initial stages of chlorination. It is believed that decreased oxidative consumption of chlorine was responsible for a major portion of the reduction of delignification as the reaction temperature was lowered. This conclusion stems from the observation that the levels of bound chlorine were not altered significantly by temperature reduction. On the other hand, the total consumption corresponded more closely to the chlorine organically bound in the pulp as temperature was reduced. This behavior implied that the oxidative reactions were more temperature sensitive than were the substitutive reactions.

Grangaard's study (21) of a balsam sulfite pulp indicated that oxidation does contribute to delignification and that this reaction is more sensitive to temperature. He employed reaction durations of three minutes up to three hours. These two conclusions can be reached from data on the chlorination of slash pine kraft pulp ranging from five to sixty minutes also (12). Eriksson and Stockman (19) have stated that oxidation is more temperature sensitive than substitution; however, no supporting data were reported. These studies lend support to the interpretation given the data obtained in chlorinations of less than one minute and suggest the observations regarding oxidative chlorine consumption are not restricted to the initial reaction phase.

It is estimated that organically bound chlorine accounted for about 50%, or less, of the total chlorine consumption during the early reaction period. Both Grangaard (21) and Chapnerkar (12) estimated that oxidation should account for 40 to 60% of the total consumption in the first 3 to 5 minutes of chlorination. Both investigators showed that oxidation accounted for increasingly larger fractions of the total reagent consumption as chlorination was extended beyond the first few minutes of reaction.

A maximum ratio of about one gram of chlorine consumed per gram of lignin removed was obtained during the first minute of chlorination. Chapnerkar (12) obtained a ratio of 1.3 for a kraft pulp and Carmody and Mears (20) reported the same ratio for a sulfite pulp. A value of about 1.5 was suggested by Giertz (18) for sulfate pulp chlorination. The lower ratio obtained in the present study is believed to result from less opportunity for secondary chlorination in the short reaction durations employed here. A practical implication of this observation is that chlorinations of short duration are more efficient as regards effective chlorine consumption.

Since oxidation increased with higher applications of chlorine, it is reasonable to expect variations in this reaction to become more influential in the overall extent of delignification. This behavior and the observed temperature sensitivity of oxidation are believed to be the cause of more pronounced sensitivity of delignification to temperature variations at a higher chlorine concentration. As noted previously, Eriksson and Stockman (19) also found that the response of kraft pulp delignification to temperature changes was affected by the chlorine dosage over a one-hour reaction period.

The response of pulp viscosity to changes in chlorinating conditions was slight except at the lowest reaction pH; however, the contribution of severe acid attack in this instance accounted for a major portion of the drastic viscosity loss.

Chlorination with hypochlorous acid alone did not yield substantial lignin removal nor chlorine consumption. Since oxidation is believed to be the primary reaction involving this acid, this reaction was ineffective in the absence of molecular chlorine. The response of a kraft pulp to hypochlorous acid treatment for long periods is not known. Possibly, the minimization of demethylation was

important as the replacement of an alkoxyl group with a hydroxyl group should promote oxidation of the aromatic ring to some degree (52).

It is believed that the accessibility of lignin to chlorine is also a factor which influences the relationship between bound chlorine and delignification. The important consideration here is the penetration of the reagent into the lignin structure. If this penetration is limited by low chlorine concentration or the position of the lignin within a fiber then secondary chlorination could occur which would not substantially improve lignin solubilization. The entry of chlorine into the lignin structure has been estimated to be of no consequence in other studies of pulp chlorination (11,21,34). However, these investigations were not confined solely to the initial reaction period where the chlorine reactions are most rapid. In addition, these studies have employed a reaction pH range where molecular chlorine is present in relatively high concentrations. The chlorination experiment at pH 1.3 in the present study also indicated that penetration of the chlorine was not of major importance in this case.

The delignification data were examined also in terms of the following rate expressions:

$$-dL/dt = k'L^a$$

and

$$k' = kf'' (C)$$

Graphical integration indicated that a was somewhat less than two in three series of experiments which included variations in chlorine concentration and temperature. Chapnerkar (12) used two reactions, both being first order with respect to lignin content, to describe delignification in an initial rapid phase and a slower reaction phase. The reaction order obtained in the present study should describe the initial phase of chlorination more closely since Chapnerkar's

approach did not include the 22 to 55% of the original which he reported as being removed "instantaneously."

The pseudo rate constant, k', was profoundly affected by changes in chlorine concentration, C. This dependence decreased as delignification progressed. No constant relationship between C and k' existed during the first 25% of lignin removal. Greater applications of chlorine yielded longer periods of variation in k' before a relatively constant value was obtained. This period of instability was most likely a product of the complex reaction system and the physical distribution of the lignin within the fiber.

It is believed that a rate expression describing delignification in the initial phase of chlorination should consider C in terms of molecular chlorine and hypochlorous acid rather than as available chlorine concentration. The results of this investigation indicated molecular chlorine concentration should be accorded greater weight as regards the rate of delignification.

The similarities observed in the comparison of PU1 and PU2 indicated that many of the conclusions drawn from the chlorination of PU1 are not restricted to this one pulp meal. Both pulp meals exhibited minor lignin removal when the presence of molecular chlorine was minimized and substantial delignification when this chlorine species was present. The reaction orders obtained by graphical differentiation were not greatly different. Definite relationships between bound chlorine and delignification were observed for both pulp meals. The somewhat lower reaction order and the more favorable relationship of chlorine content and lignin removal obtained with PU2 are believed to result from a difference in the accessibility of the lignin to chlorine in the two pulp meals.

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